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cis-Alkoxyspiro-substituted tetramic acid derivatives

The invention relates to novel cis-alkoxyspiro-substituted tetramic acid derivatives, to a plurality of processes and intermediates for their preparation and to their use as pesticides and/or herbicides. Moreover, the invention relates to novel selective herbicidal combinations of active compounds comprising firstly cis-alkoxyspiro-substituted tetramic acid derivatives and secondly a crop plant compatibility-improving compound, which combinations can be used with particularly good results for the selective control of weeds in various crops of useful plants.

3-Acylpyrrolidine-2,4-diones are described as having pharmaceutical properties (S. Suzuki et al. Chem. Pharm. Bull. <u>15</u> 1120 (1967)). Furthermore, N-phenylpyrrolidine-2,4-diones were synthesized by R. Schmierer and H. Mildenberger (Liebigs Ann. Chem. <u>1985</u>, 1095). A biological activity of these compounds has not been described.

EP-A-0 262 399 and GB-A-2 266 888 disclose compounds of a similar structure (3-aryl-pyrrolidine-2,4-diones); however, a herbicidal, insecticidal or acaricidal action of these compounds has hitherto not been described. Unsubstituted bicyclic 3-arylpyrrolidine-2,4-dione derivatives (EP-A-355 599 and EP-A-415 211) and substituted monocyclic 3-arylpyrrolidine-2,4-dione derivatives (EP-A-377 893 and EP-A-442 077) having herbicidal, insecticidal or acaricidal action are known.

Also known are polycyclic 3-arylpyrrolidine-2,4-dione derivatives (EP-A-442 073) and 1H-EP-A-596 298, 20 arylpyrrolidinedione derivatives (EP-A-456 063, EP-A-521 334, EP-A-613 885, WO 94/01 997, WO 93/26954, WO 95/20 572, EP-A-613 884, WO 97/02 243, EP-A 0 668 267, WO 96/25 395, WO 96 35 664, WO 97/01 535, WO 98/25928, WO 98/05638, WO 98/06721, WO 97/36 868, WO 97/43275, WO 99/55673, WO 99/16748, WO 99/24437, WO 99/43649, WO 99/48869, WO 01/09092, WO 01/17972, WO 01/23354, WO 01/74770 and WO 03/013249). 25

As a result of the preparative processes, the known compounds are obtained in the form of cis/trans isomer mixtures with varying cis/trans ratios.

However, in particular at low application rates and concentrations, the activity and the activity spectrum of these compounds are not always entirely satisfactory.

Moreover, the compatibility with plants of these compounds is not always sufficient.

This invention now provides novel compounds of the formula (I)

$$AO \bigvee_{H} \bigcirc X$$
 (I)

in which

5 X represents C₂-C₄-alkyl,

Y represents halogen and

Z represents C_1 - C_4 -alkyl,

A represents alkyl,

G represents hydrogen (a) or represents

$$R^{1}$$
 (b), R^{2} (c), SO_{2} R^{3} (d), R^{6} R^{5} (e), R^{5} (e), R^{6} R^{7} (g),

10

in which

- E represents a metal ion equivalent or an ammonium ion,
- L represents oxygen or sulphur,
- M represents oxygen or sulphur,
- 15 R¹ represents in each case optionally substituted alkyl, alkenyl, alkoxyalkyl, alkylthioalkyl or polyalkoxyalkyl or represents cycloalkyl or heterocyclyl, each of which is optionally substituted by halogen, alkyl or alkoxy, or

represents in each case optionally substituted phenyl, hetaryl, phenyl-C₁-C₄-alkyl, phenyl-C₁-C₂-alkenyl or hetaryl-C₁-C₄-alkyl,

- R² represents in each case optionally halogen-substituted alkyl, alkenyl, alkoxyalkyl or polyalkoxyalkyl or represents in each case optionally substituted cycloalkyl, phenyl or benzyl,
- R³, R⁴ and R⁵ independently of one another represent in each case optionally halogen-substituted alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkenylthio or cycloalkylthio or represent in each case optionally substituted phenyl, benzyl, phenoxy or phenylthio,
- 10 R⁶ and R⁷ independently of one another represent hydrogen, represent in each case optionally halogen-substituted alkyl, cycloalkyl, alkenyl, alkoxy, alkoxyalkyl, represent in each case optionally substituted phenyl or benzyl, or together with the N atom to which they are attached form an optionally substituted cycle which optionally contains oxygen or sulphur.
- Including the different meanings (a), (b), (c), (d), (e), (f) and (g) of group G, the following principal structures (I-a) to (I-g) (cis-isomer) result:

AO
$$Z$$
 (Ib),

AO
$$\mathbb{R}^2$$
-M \mathbb{Z} (Ic),

AO
$$R^3$$
-SO₂-O Z (Id),

AO
$$\mathbb{R}^4$$
 \mathbb{R}^5 \mathbb{R}^5

AO
$$Z$$
 (Ig)

in which

5

A, E, L, M, X, Y, Z, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are as defined above.

Furthermore, it has been found that the novel compounds of the formula (I) are obtained by one of the processes described below:

(A) compounds of the formula (I-a),

5 in which

A, X, Y and Z are as defined above

are obtained when

compounds of the formula (II),

$$AO \xrightarrow{\text{CO}_2 R^8} X \qquad \text{(II)}$$

in which

15

A, X, Y and Z are as defined above

and

 R^8 represents alkyl (preferably C_1 - C_6 -alkyl),

are condensed intramolecularly in the presence of a diluent and in the presence of a base.

(B) compounds of the formula (I-b) shown above in which A, R¹, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, X, Y and Z are as defined above are reacted

α) with acid halides of the formula (III),

in which

R¹ is as defined above and

5 Hal represents halogen (in particular chlorine or bromine)

or

B) with carboxylic anhydrides of the formula (IV),

$$R^1$$
-CO-O-CO- R^1 (IV)

in which

10 R¹ is as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

(C) compounds of the formula (I-c) shown above in which A, R², M, X, Y and Z are as defined above and L represents oxygen are obtained when compounds of the formula (I-a) shown above in which A, X, Y and Z are as defined above are in each case reacted

with chloroformic esters or chloroformic thioesters of the formula (V),

$$R^2$$
-M-CO-Cl (V)

in which

20 R² and M are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

- (D) compounds of the formula (I-c) shown above in which A, R², M, X, Y and Z are as defined above and L represents sulphur are obtained when compounds of the formula (I-a) shown above in which A, X, Y and Z are as defined above are in each case reacted
- 5 α) with chloromonothioformic esters or chlorodithioformic esters of the formula (VI),

$$CI \underset{S}{\bigvee} M-R^2$$
 (VI)

in which

M and R² are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder,

or

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B) with carbon disulphide and then with compounds of the formula (VII),

in which

15 R² is as defined above and

Hal represents chlorine, bromine or iodine,

if appropriate in the presence of a diluent and if appropriate in the presence of a base.

(E) compounds of the formula (I-d) as shown above in which A, R³, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, X, Y and Z are as defined above are in each case reacted

with sulphonyl chlorides of the formula (VIII),

$$R^3$$
-SO₂-Cl (VIII)

in which

R³ is as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

5 (F) compounds of the formula (I-e) shown above in which A, L, R⁴, R⁵, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) as shown above in which A, X, Y and Z are as defined above are in each case reacted

with phosphorus compounds of the formula (IX),

$$Hal - P$$

$$L R^{5}$$

$$(IX)$$

in which

L, R⁴ and R⁵ are as defined above and

Hal represents halogen (in particular chlorine or bromine),

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

15 (G) compounds of the formula (I-f) shown above in which A, E, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, X, Y and Z are as defined above are in each case reacted

with metal compounds or amines of the formulae (X) or (XI), respectively,

$$R^{10} \sim R^{8}$$
 $N \sim R^{8}$
 $R^{10} \sim R^{8}$
 $R^{10} \sim R^{8}$
 $R^{10} \sim R^{10}$
 $R^{10} \sim R^{10}$

20 in which

Me represents a mono- or divalent metal (preferably an alkali metal or alkaline earth metal, such as lithium, sodium, potassium, magnesium or calcium),

- t represents the number 1 or 2 and
- R⁸, R⁹, R¹⁰ independently of one another represent hydrogen or alkyl (preferably C₁-C₈-alkyl),

if appropriate in the presence of a diluent.

- (H) compounds of the formula (I-g) shown above in which A, L, R⁶, R⁷, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, X, Y and Z are as defined above are in each case reacted
- 10 α) with isocyanates or isothiocyanates of the formula (XII),

$$R^6$$
-N=C=L (XII)

in which

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R⁶ and L are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of a catalyst, or

B) with carbamoyl chlorides or thiocarbamoyl chlorides of the formula (XIII),

$$R^6$$
 N CI $(XIII)$

in which

L, R⁶ and R⁷ are as defined above,

20 if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

(I) compounds of the formulae (I-a) to (I-g) shown above are obtained when cis/trans isomer mixtures of the formulae (I-a') to (I-g'), known, for example, from EP-A-835 243,

$$A-Ow \bigvee_{OH} \bigvee_{Z} \bigvee_{(I-a')}$$

$$A-Ow \bigvee_{Q = \mathbb{Z}^{1}} \bigvee_{Z} \bigvee_{(I-b')}$$

$$A-Ow \longrightarrow \begin{array}{c} H \longrightarrow O \\ X \longrightarrow \\ L \longrightarrow O \end{array}$$

$$L \longrightarrow \begin{array}{c} X \longrightarrow \\ Z \longrightarrow \\ M-R^2 \end{array}$$

$$(I-c')$$

$$A-O \longrightarrow \begin{array}{c} H & O \\ \hline N & O \\ \hline R^3-SO_2-O \\ \hline Z \end{array} \qquad (I-d')$$

$$A-Ow \longrightarrow H \longrightarrow V$$

$$R^{4} \longrightarrow V \longrightarrow V$$

$$R^{5} \longrightarrow V \longrightarrow V$$

$$(I-e')$$

$$A-Ow \bigvee_{E-O} \bigvee_{Z} \bigvee_{(I-f')}$$

$$A-Ow \bigcup_{L} \bigvee_{Q} \bigvee_{Z} \bigvee_{Q} \bigvee_{Q} \bigvee_{(I-g')} \bigvee_{Q} \bigvee_{Q}$$

in which

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A, E, L, M X, Y, Z, R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are as defined above are separated using physical separation processes, such as, for example, column chromatography or fractional crystallization.

(J) furthermore, it has been found that compounds of the formula (I-a) are obtained when compounds of the formulae (I-b), (I-c), (I-d), (I-e), (I-f) or (I-g) in which A, E, L, M, X, Y, Z, R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are as defined above are hydrolysed using, for example, aqueous bases and then acidified.

In April 2002, the following compounds of the formula (I-a') were disclosed during the European Patent Examination proceedings relating to EP-A-835 243:

$$A-O OH$$
 Z
 $(I-a')$

Subsequently filed as Ex. No. in EP	Х	Y	Z	A	m.p. °C
I-1-a-40	C₂H₅	Br	CH ₃	СН₃	>220

I-1-a-43	C ₂ H ₅	Br	CH ₃	C ₂ H ₅	136
I-1-a-44	C ₂ H ₅	Br	C ₂ H ₅	CH ₃	208
I-1-a-55	C ₂ H ₅	Ci	CH₃	CH ₃	>244
I-1-a-56	C ₂ H ₅	Cl	C ₂ H ₅	CH ₃	241

Furthermore, it has been found that the novel compounds of the formula (I) are highly active pesticides, preferably insecticides and/or acaricides, and/or herbicides.

Surprisingly, it has now also been found that certain substituted cyclic ketoenols, when used together with the crop plant compatibility-improving compounds (safeners/antidotes) described below, are highly suitable for preventing damage to the crop plants and can be used particularly advantageously as broad-spectrum effective combination preparations for the selective control of unwanted plants in crops of useful plants, such as, for example, in cereals, but also maize, soya beans and rice.

10 The invention also provides selective herbicidal compositions comprising an effective amount of a combination of active compounds comprising the components

(a') at least one substituted cyclic ketoenol of the formula (I) in which A, G, X, Y and Z are as defined above

and

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15 (b') at least one crop plant compatibility-improving compound from the following group of compounds:

1-dichloro-4-dichloroacetyl-1-oxa-4-azaspiro[4.5]decane MON-4660), (AD-67, acetylhexahydro-3,3,8a-trimethylpyrrolo[1,2-a]pyrimidin-6(2H)-one BAS-(dicyclonon, 4-dichloroacetyl-3,4-dihydro-3-methyl-2H-1,4-benzoxazine (benoxacor), 145138), 1-methylhexyl 5-chloroquinoline-8-oxyacetate (cloquintocet-mexyl - cf. also related compounds in EP-A-86750, EP-A-94349, EP-A-191736, EP-A-492366), 3-(2chlorobenzyl)-1-(1-methyl-1-phenylethyl)urea (cumyluron), α-(cyanomethoximino)phenylacetonitrile (cyometrinil), 2,4-dichlorophenoxyacetic acid (2,4-D), 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB), 1-(1-methyl-1-phenylethyl)-3-(4-

methylphenyl)urea (daimuron, dymron), 3,6-dichloro-2-methoxybenzoic acid (dicamba), S-1-methyl 1-phenylethyl piperidine-1-thiocarboxylate (dimepiperate), 2,2-dichloro-N-(2oxo-2-(2-propenylamino)ethyl)-N-(2-propenyl)acetamide (DKA-24), 2,2-dichloro-N,N-di-2-propenylacetamide (dichlormid), 4,6-dichloro-2-phenylpyrimidine (fenclorim), ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl-1H-1,2,4-triazole-3-carboxylate (fenchlorazole-ethyl 5 - cf. also related compounds in EP-A-174562 and EP-A-346620), phenylmethyl 2-chloro-4trifluoromethylthiazole-5-carboxylate (flurazole), 4-chloro-N-(1,3-dioxolan-2-ylmethoxy)-3-dichloroacetyl-5-(2-furanyl)-2,2oxime (fluxofenim), a-trifluoroacetophenone 4,5-dihydro-5,5-diphenyl-3-(furilazole, MON-13900), ethyl dimethyloxazolidine isoxazolecarboxylate (isoxadifen-ethyl - cf. also related compounds in WO-A-95/07897), 1-10 3,6-dichloro-2-methoxybenzoate (lactidichlor), (4-chloro-o-(ethoxycarbonyl)ethyl tolyloxy)acetic acid (MCPA), 2-(4-chloro-o-tolyloxy)propionic acid (mecoprop), diethyl 1-(2,4-dichorophenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3,5-dicarboxylate (mefenpyr-diethyl - cf. also related compounds in WO-A-91/07874), 2-dichloromethyl-2-methyl-1,3-dioxolane (MG-838), 1-oxa-4-azaspiro[4.5]decane-4-carbodithioate 15 (MG-191), 2-propenyl 1,8-naphthalic anhydride, α-(1,3-dioxolan-2-ylmethoximino)phenylacetonitrile (oxabetrinil), 2,2-dichloro-N-(1,3-dioxolan-2-ylmethyl)-N-(2-propenyl)acetamide (PPG-1292), 3-dichloroacetyl-3-dichloroacetyl-2,2-dimethyloxazolidine (R-28725),4-(4-chloro-o-tolyl)butyric acid, 4-(4-chloro-2,2,5-trimethyloxazolidine (R-29148), phenoxy)butyric acid, diphenylmethoxyacetic acid, methyl diphenylmethoxyacetate, ethyl 20 diphenylmethoxyacetate, methyl 1-(2-chlorophenyl)-5-phenyl-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichlorophenyl)-5-methyl-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichloro-1-(2,4-dichlorophenyl)-5-(1,1-diphenyl)-5-isopropyl-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichlorophenyl)-5-phenylethyl methylethyl)-1H-pyrazole-3-carboxylate, compounds in EP-A-269806 related 1H-pyrazole-3-carboxylate (cf. also 25 EP-A-333131), ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate, ethyl 5-phenyl-2-isoxazoline-3-carboxylate, ethyl 5-(4-fluorophenyl)-5-phenyl-2-isoxazoline-3-carboxylate (cf. also related compounds in WO-A-91/08202), 1,3-dimethylbut-1-yl 5-chloroquinoline-8-1-allyloxyprop-2-yl 5-chloroquinoline-8-oxyacetate, 4-allyloxybutyl oxyacetate, ethyl 5-chloroquinoxaline-8-oxyacetate, methyl 5-chloroquinoline-8-oxyacetate, 30 allyl 5-chloroquinoxaline-8-oxyacetate, 2-oxoprop-1-yl 5-chloroquinoline-8-oxyacetate. diallyl 5-chloroquinoline-8-oxymalonate, diethyl 5-chloroquinoline-8-oxyacetate, 5-chloroquinoxaline-8-oxymalonate, diethyl 5-chloroquinoline-8-oxymalonate (cf. also related compounds in EP-A-582198), 4-carboxychroman-4-ylacetic acid (AC-304415, cf. 4-chlorophenoxyacetic acid, 3,3'-dimethyl-4-methoxybenzophenone, EP-A-613618), 1-bromo-4-chloromethylsulphonylbenzene, 1-[4-(N-2-methoxybenzoylsulphamoyl)phenyl]-N-(2-methoxybenzoyl)-4-[(methylaminocarbonyl)-3-methylurea (also known as 1-[4-(N-2-methoxybenzoylsulphamoyl)phenyl]-3,3-diamino]benzenesulphonamide), 1-[4-(N-4,5-dimethylbenzoylsulphamoyl)phenyl]-3-methylurea, methylurea, 1-[4-(N-naphthylsulphamoyl)phenyl]-3,3-dimethylurea, N-(2-methoxy-5-methylbenzoyl)-4-(cyclopropylaminocarbonyl)benzenesulphonamide,

and/or one of the following compounds, defined by general formulae,

10 of the general formula (IIa)

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$$(X^1)_m$$
 R^{12} (IIa)

or of the general formula (IIb)

$$X^3$$
 X^2
 X^2
 X^2
 X^3
 X^3

or of the formula (IIc)

$$R^{14}
\downarrow N R^{15}$$
(IIc)

15

where

m represents a number 0, 1, 2, 3, 4 or 5,

A¹ represents one of the divalent heterocyclic groupings shown below,

n represents a number 0, 1, 2, 3, 4 or 5,

A² represents optionally C₁-C₄-alkyl- and/or C₁-C₄-alkoxycarbonyl-substituted alkanediyl having 1 or 2 carbon atoms,

5 R¹² represents hydroxyl, mercapto, amino, C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino or di-(C₁-C₄-alkyl)amino,

R¹³ represents hydroxyl, mercapto, amino, C₁-C₇-alkoxy, C₁-C₆-alkenyloxy, C₁-C₆-alkenyloxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino or di-(C₁-C₄-alkyl)-amino,

R¹⁴ represents in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₄-alkyl,

R¹⁵ represents hydrogen, in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, dioxolanyl-C₁-C₄-alkyl, furyl, furyl-C₁-C₄-alkyl, thienyl, thiazolyl, piperidinyl, or optionally fluorine-, chlorine- and/or bromine- or C₁-C₄-alkyl-substituted phenyl,

represents hydrogen, in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, dioxolanyl-C₁-C₄-alkyl, furyl, furyl-C₁-C₄-alkyl, thienyl, thiazolyl, piperidinyl, or optionally fluorine-, chlorine- and/or bromine- or C₁-C₄-alkyl-substituted phenyl, or together R¹⁵ and R¹⁶ represent also C₃-C₆-alkanediyl or C₂-C₅-oxaalkanediyl, each of which is optionally substituted by C₁-C₄-alkyl, phenyl, furyl, a fused benzene ring or by two substituents which, together with the C atom to which they are attached, form a 5-or 6-membered carbocycle,

R¹⁷ represents hydrogen, cyano, halogen, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₄-alkyl, C₃-C₆-cycloalkyl or phenyl,

R¹⁸ represents hydrogen or optionally hydroxyl-, cyano-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, C₃-C₆-cycloalkyl or tri(C₁-C₄-alkyl)silyl,

- R¹⁹ represents hydrogen, cyano, halogen, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₄-alkyl, C₃-C₆-cycloalkyl or phenyl,
- 5 X¹ represents nitro, cyano, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkyl, C₁-C₄-alkoxy,
 - X² represents hydrogen, cyano, nitro, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy,
- represents hydrogen, cyano, nitro, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy,

and/or the following compounds, defined by general formulae,

of the general formula (IId)

$$O \xrightarrow{R^{21}} (X^5)_v \xrightarrow{R^{20}} (X^4)_t$$

$$SO_2 \xrightarrow{N} O$$
(IId)

or of the general formula (IIe)

$$R^{23} \xrightarrow{N} (X^5)_v$$

$$SO_2 \xrightarrow{N} (X^4)_t$$
(IIe)

15

where

- t represents a number 0, 1, 2, 3, 4 or 5,
- v represents a number 0, 1, 2, 3, 4 or 5,

- R²⁰ represents hydrogen or C₁-C₄-alkyl,
- R²¹ represents hydrogen or C₁-C₄-alkyl,
- represents hydrogen, in each case optionally cyano-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino or di-(C₁-C₄-alkyl)amino, or in each case optionally cyano-, halogen- or C₁-C₄-alkyl-substituted C₃-C₆-cycloalkyl, C₃-C₆-cycloalkyloxy, C₃-C₆-cycloalkylthio or C₃-C₆-cycloalkylamino,
 - R²³ represents hydrogen, optionally cyano-, hydroxyl-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, in each case optionally cyano- or halogen-substituted C₃-C₆-alkenyl or C₃-C₆-alkynyl, or optionally cyano-, halogen- or C₁-C₄-alkyl-substituted C₃-C₆-cycloalkyl,
- represents hydrogen, optionally cyano-, hydroxyl-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, in each case optionally cyano- or halogen-substituted C₃-C₆-alkenyl or C₃-C₆-alkynyl, optionally cyano-, halogen- or C₁-C₄-alkyl-substituted C₃-C₆-cycloalkyl, or optionally nitro-, cyano-, halogen-, C₁-C₄-alkyl-, C₁-C₄-haloalkyl-, C₁-C₄-alkoxy- or C₁-C₄-haloalkoxy-substituted phenyl, or together with R²³ represents in each case optionally C₁-C₄-alkyl-substituted C₂-C₆-alkanediyl or C₂-C₅-oxaalkanediyl,
 - x⁴ represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy, and
 - x⁵ represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy.
- The formula (I) provides a general definition of the compounds according to the invention. Preferred substituents or ranges of the radicals listed in the formulae given above and below are illustrated below:
 - X preferably represents ethyl, n-propyl or n-butyl,
 - Y preferably represents halogen,
- 25 Z <u>preferably</u> represents methyl, ethyl or n-propyl,
 - A <u>preferably</u> represents C₁-C₆-alkyl,

G preferably represents hydrogen (a) or represents one of the groups

in which

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- E represents a metal ion equivalent or an ammonium ion,
- L represents oxygen or sulphur and
 - M represents oxygen or sulphur,
- R¹ preferably represents C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₆-alkoxy-C₁-C₆-alkyl, C₁-C₆-alkyl or poly-C₁-C₄-alkoxy-C₁-C₄-alkyl, each of which is optionally mono- to heptasubstituted by halogen, mono- or disubstituted by cyano,

monosubstituted by -CO-R¹¹, -C=N-OR¹¹, -CO₂R¹¹ or CO-N R¹¹, or represents

 C_3 - C_8 -cycloalkyl which is optionally mono- to trisubstituted by halogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkoxy and in which optionally one or two not directly adjacent methylene groups are replaced by oxygen and/or sulphur,

represents phenyl, phenyl- C_1 - C_2 -alkyl or phenyl- C_1 - C_2 -alkenyl, each of which is optionally mono- to trisubstituted by halogen, cyano, nitro, C_1 - C_6 -alkyl, C_1 - C_6 -alkyl, C_1 - C_6 -alkylsulphinyl or C_1 - C_6 -alkylsulphonyl,

represents 5- or 6-membered hetaryl which is optionally mono- or disubstituted by halogen or C₁-C₆-alkyl and has one or two heteroatoms from the group consisting of oxygen, sulphur and nitrogen,

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R² <u>preferably</u> represents C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₆-alkoxy-C₂-C₆-alkyl or poly-C₁-C₆-alkoxy-C₂-C₆-alkyl, each of which is optionally mono- to trisubstituted by halogen,

represents C_3 - C_8 -cycloalkyl which is optionally mono- or disubstituted by halogen, C $_1$ - C_6 -alkyl or C_1 - C_6 -alkoxy, or

represents phenyl or benzyl, each of which is optionally mono- to trisubstituted by halogen, cyano, nitro, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkyl or C₁-C₆-haloalkoxy,

preferably represents C₁-C₈-alkyl which is optionally mono- or polysubstituted by halogen or represents phenyl or benzyl, each of which is optionally mono- or disubstituted by halogen, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy, cyano or nitro,

R⁴ and R⁵ independently of one another <u>preferably</u> represent C₁-C₈-alkyl, C₁-C₈-alkoxy, C₁-C₈-alkylamino, di-(C₁-C₈-alkyl)amino, C₁-C₈-alkylthio or C₂-C₈-alkenylthio, each of which is optionally mono- to trisubstituted by halogen, or represent phenyl, phenoxy or phenylthio, each of which is optionally mono- to trisubstituted by halogen, nitro, cyano, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkylhio, C₁-C₄-alkylthio, C₁-C₄-haloalkyl,

R⁶ and R⁷ independently of one another <u>preferably</u> represent hydrogen, represent C₁-C₈20 alkyl, C₃-C₈-cycloalkyl, C₁-C₈-alkoxy, C₃-C₈-alkenyl or C₁-C₈-alkoxy-C₂-C₈-alkyl,
each of which is optionally mono- to trisubstituted by halogen, represent phenyl or
benzyl, each of which is optionally mono- to trisubstituted by halogen, C₁-C₈-alkyl,
C₁-C₈-haloalkyl or C₁-C₈-alkoxy, or together represent a C₃-C₆-alkylene radical
which is optionally mono- or disubstituted by C₁-C₄-alkyl and in which optionally
one methylene group is replaced by oxygen or sulphur,

R¹¹ preferably represents hydrogen or represents C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl or C₁-C₄-alkoxy-C₂-C₄-alkyl, each of which is optionally monotor trisubstituted by halogen, or represents C₃-C₆-cycloalkyl which is optionally monoor disubstituted by halogen, C₁-C₂-alkyl or C₁-C₂-alkoxy and in which optionally one

or two not directly adjacent methylene groups are replaced by oxygen or represents phenyl or phenyl-C₁-C₃-alkyl, each of which is optionally mono- or disubstituted by halogen, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy, cyano or nitro,

5 R^{11'} preferably represents hydrogen, C₁-C₆-alkyl or C₃-C₆-alkenyl.

In the radical definitions mentioned as being preferred, halogen represents fluorine, chlorine, bromine and iodine, in particular fluorine, chlorine and bromine.

- X particularly preferably represents ethyl or n-propyl,
- Y particularly preferably represents chlorine or bromine,
- 10 Z particularly preferably represents methyl or ethyl,
 - A particularly preferably represents methyl, ethyl, n-propyl, n-butyl or isobutyl,
 - G particularly preferably represents hydrogen (a) or represents one of the groups

in which

- 15 E represents a metal ion equivalent or an ammonium ion,
 - L represents oxygen or sulphur and
 - M represents oxygen or sulphur,
- particularly preferably represents C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₁-C₄-alkoxy-C₁-C₂-alkyl, C₁-C₄-alkylthio-C₁-C₂-alkyl or poly-C₁-C₃-alkoxy-C₁-C₂-alkyl, each of which is optionally mono- to pentasubstituted by fluorine or chlorine, monosubstituted by cyano, monosubstituted by -CO-R¹¹, -C=N-OR¹¹ or CO₂R¹¹, or represents C₃-C₆-

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cycloalkyl which is optionally mono- or disubstituted by fluorine, C₁-C₂-alkyl or C₁-C₂-alkoxy and in which optionally one or two not directly adjacent methylene groups are replaced by oxygen,

represents phenyl or benzyl, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine, cyano, nitro, C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulphonyl, C₁-C₄-alkylsulphinyl, C₁-C₂-haloalkyl or C₁-C₂-haloalkoxy,

represents pyrazolyl, thiazolyl, pyridyl, pyrimidyl, furanyl or thienyl, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine or C₁-C₂-alkyl,

R² particularly preferably represents C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₁-C₄-alkoxy-C₂-C₄
alkyl or poly-C₁-C₄-alkoxy-C₂-C₄-alkyl, each of which is optionally monot to trisubstituted by fluorine or chlorine,

represents C_3 - C_7 -cycloalkyl which is optionally monosubstituted by C_1 - C_2 -alkyl or C_1 - C_2 -alkoxy or

represents phenyl or benzyl, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine, cyano, nitro, C₁-C₄-alkyl, methoxy, trifluoromethyl or trifluoromethoxy,

R³ particularly preferably represents C₁-C₄-alkyl which is optionally monot to trisubstituted by fluorine or chlorine or represents phenyl or benzyl, each of which is optionally monosubstituted by fluorine, chlorine, bromine, C₁-C₄-alkyl, C₁-C₄-alkoxy, trifluoromethyl, trifluoromethoxy, cyano or nitro,

R⁴ and R⁵ independently of one another <u>particularly preferably</u> represent C₁-C₆-alkyl, C₁-C₆-alkyl, C₁-C₆-alkylamino, di-(C₁-C₆-alkyl)amino, C₁-C₆-alkylthio or C₃-C₄-alkenylthio, each of which is optionally mono- to trisubstituted by fluorine or chlorine, or represent phenyl, phenoxy or phenylthio, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine, nitro, cyano, C₁-C₃-alkoxy, trifluoromethoxy, C₁-C₃-alkylthio, C₁-C₃-alkyl or trifluoromethyl,

R⁶ and R⁷ independently of one another <u>particularly preferably</u> represent hydrogen, represent C₁-C₆-alkyl, C₃-C₆-cycloalkyl, C₁-C₄-alkoxy, C₃-C₆-alkenyl or C₁-C₆-

alkoxy-C₂-C₆-alkyl, each of which is optionally mono- to trisubstituted by fluorine or chlorine, represent phenyl which is optionally mono- or disubstituted by fluorine, chlorine, bromine, trifluoromethyl, C₁-C₄-alkyl or C₁-C₄-alkoxy, or together represent a C₅-C₆-alkylene radical which is optionally mono- or disubstituted by methyl and in which optionally one methylene group is replaced by oxygen,

R¹¹ particularly preferably represents C₁-C₄-alkyl, C₃-C₄-alkenyl, C₃-C₄-alkynyl or C₁-C₄-alkoxy-C₂-C₃-alkyl or represents C₃-C₆-cycloalkyl in which optionally one methylene group is replaced by oxygen.

In the radical definitions mentioned as being particularly preferred, halogen represents fluorine, chlorine and bromine, in particular fluorine and chlorine.

- X very particularly preferably represents ethyl or n-propyl, (especially ethyl)
- Y very particularly preferably represents chlorine or bromine,
- Z very particularly preferably represents methyl or ethyl,
- A <u>very particularly preferably</u> represents methyl, ethyl or n-propyl, (especially ethyl or methyl),
 - G very particularly preferably represents hydrogen (a) or represents one of the groups

$$\bigcap_{R^1} (b), \qquad \bigcup_{M} R^2 (c), \qquad \bigcup_{N} R^7 (g)$$
(especially hydrogen a) or one of groups (b) or (c)),

in which

20 L represents oxygen and

M represents oxygen or sulphur (especially oxygen),

R¹ very particularly preferably represents C₁-C₆-alkyl, C₂-C₆-alkenyl, C₁-C₂-alkoxy-C₁-C₂-alkyl, C₁-C₂-alkylthio-C₁-C₂-alkyl or poly-C₁-C₂-alkoxy-C₁-C₂-alkyl, each of which is optionally mono- to trisubstituted by fluorine or chlorine, or represents

cyclopropyl, cyclopentyl or cyclohexyl, each of which is optionally monosubstituted by fluorine, chlorine, methyl, ethyl or methoxy,

represents phenyl which is optionally monosubstituted by fluorine, chlorine, bromine, cyano, nitro, methyl, ethyl, n-propyl, isopropyl, methoxy, ethoxy, methylthio, ethylthio, methylsulphinyl, ethylsulphinyl, methylsulphonyl, ethylsulphonyl, trifluoromethyl or trifluoromethoxy,

represents furanyl, thienyl or pyridyl, each of which is optionally monosubstituted by chlorine, bromine or methyl,

R² <u>very particularly preferably</u> represents C₁-C₈-alkyl, C₂-C₆-alkenyl or C₁-C₃-alkoxy-10 C₂-C₃-alkyl, cyclopentyl or cyclohexyl,

or represents phenyl or benzyl, each of which is optionally monosubstituted by fluorine, chlorine, bromine, cyano, nitro, methyl, methoxy, trifluoromethyl or trifluoromethoxy,

- R⁶ very particularly preferably represents hydrogen, represents C₁-C₄-alkyl, C₃-C₆cycloalkyl or allyl, represents phenyl which is optionally monosubstituted by fluorine, chlorine, bromine, methyl, methoxy or trifluoromethyl,
 - R⁷ very particularly preferably represents methyl, ethyl, n-propyl, isopropyl or allyl,
 - R⁶ and R⁷ together <u>very particularly preferably</u> represent a C₅-C₆-alkylene radical in which optionally one methylene group is replaced by oxygen.
- The general or preferred radical definitions or illustrations listed above can be combined with one another as desired, i.e. including combinations between the respective ranges and preferred ranges. They apply to the end products and, correspondingly, to the precursors and intermediates.
- Preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being preferred (preferable).

<u>Particular preference</u> according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being particularly preferred.

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<u>Very particular preference</u> according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being very particularly preferred.

Saturated or unsaturated hydrocarbon radicals, such as alkyl, alkanediyl or alkenyl, can in each case be straight-chain or branched as far as this is possible, including in combination with heteroatoms, such as, for example, in alkoxy.

Optionally substituted radicals can be mono- or polysubstituted, where in the case of polysubstitutions the substituents can be identical or different.

In addition to the compounds mentioned in the Preparation Examples, the following compounds of the formulae (I-a), (I-b) and (I-c) may be specifically mentioned:

AO
$$C_2H_5$$
 (I-a)

Y \mathbf{Z} A Cl CH₃ CH₃ CH_3 Cl C_2H_5 CH_3 CH_3 Br C_2H_5 CH_3 Br Cl CH_3 C_2H_5 C_2H_5 Cl C_2H_5 CH₃ C_2H_5 Br C_2H_5 Br C_2H_5 Cl CH₃ C_3H_7 Cl C_2H_5 C_3H_7 CH_3 C_3H_7 Br C_2H_5 C_3H_7 Br

$$A \xrightarrow{\text{O}} Z \xrightarrow{\text{(I-b)}}$$

<u>Table 1</u> $A = CH_3$

X	Y	Z	R ¹
C ₂ H ₅	Cl	CH ₃	CH ₃
C ₂ H ₅	Cl	CH ₃	C ₂ H ₅
C ₂ H ₅	Cl	CH ₃	C ₃ H ₇
C ₂ H ₅	Cl	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Cl	CH ₃	C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Cl	СН3	t-C ₄ H ₉
C ₂ H ₅	Cl	СН3	\triangleright
C ₂ H ₅	Cl	CH ₃	H ₃ C-O-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₅ C ₂ -O-CH ₂
C ₂ H ₅	Cl	СН3	H₃C-S-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₅ C ₂ -S-CH ₂

5 Table 2: A, X and R^1 are as given in Table 1 $Y = Cl, Z = C_2H_5$

Table 3: A, X and R^1 are as given in Table 1 $Y = Br, Z = CH_3$

Table 4: A, X, and R^1 are as given in Table 1 $Y = Br, Z = C_2H_5$

$$A \xrightarrow{O} Z \xrightarrow{X} Y \qquad (I-b)$$

 $\underline{\textbf{Table 5}} \qquad \qquad A = C_2 H_5$

X	Y	Z	R ¹
7.	_		
C ₂ H ₅	Cl	CH ₃	CH ₃
C ₂ H ₅	Cl	CH ₃	C ₂ H ₅
C ₂ H ₅	Cl	CH ₃	С ₃ Н ₇
C ₂ H ₅	Cl	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Cl	CH ₃	C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	<u></u>
C ₂ H ₅	Cl	CH ₃	H ₃ C-O-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₅ C ₂ -O-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₃ C ₂ -S-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₅ C ₂ -S-CH ₂

<u>Table 6:</u> A, X and R^1 are as given in Table 5 Y = Cl, $Z = C_2H_5$

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<u>Table 7:</u> A, X and R¹ are as given in Table 5

$$Y = Br, Z = CH_3$$

Table 8: A, X, and R^1 are as given in Table 5 $Y = Br, Z = C_2H_5$

$$A \xrightarrow{\text{O}} Z \xrightarrow{\text{II-b}}$$

5 Table 9 $A = C_3H_7$

X	Y	Z	R ¹
C ₂ H ₅	Cl	CH ₃	CH ₃
C ₂ H ₅	Cl	CH ₃	C ₂ H ₅
C ₂ H ₅	Cl	CH ₃	C ₃ H ₇
C ₂ H ₅	Cl	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Cl	CH ₃	C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Cl	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Cl	СН3	
C ₂ H ₅	Cl	CH ₃	H ₃ C-O-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₅ C ₂ -O-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₃ C ₂ -S-CH ₂
C ₂ H ₅	Cl	CH ₃	H ₅ C ₂ -S-CH ₂

Table 10: A, X and R^1 are as given in Table 9 Y = Cl, $Z = C_2H_5$

Table 11: A, X and R^1 are as given in Table 9 Y = Br, $Z = CH_3$

Table 12: A, X, and R^1 are as given in Table 9 $Y = Br, Z = C_2H_5$

 $\underline{\textbf{Table 13}} \qquad A = CH_3 \qquad M = O$

5

X	Y	Z	R ¹
C ₂ H ₅	Br	CH ₃	CH ₃
C ₂ H ₅	Br	CH ₃	C ₂ H ₅
C ₂ H ₅	Br	CH ₃	C ₃ H ₇
C ₂ H ₅	Br	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Br	CH ₃	C ₄ H ₉
C ₂ H ₅	Br	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉ -CH ₂
C ₂ H ₅	Br	CH ₃	C ₆ H ₅ -CH ₂
C₂H₅	Br	CH ₃	C ₆ H ₅

Table 14: A, X, M and R^2 are as given in Table 13 Y = Br, $Z = C_2H_5$ <u>Table 15:</u> A, X, M and R^2 are as given in Table 13 Y = Cl, $Z = CH_3$

Table 16: A, X, M and R^2 are as given in Table 13 Y = Cl, $Z = C_2H_5$

 $\underline{\textbf{Table 17}} \qquad \quad A = C_2 H_5 \qquad \quad M = O$

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X	Y	Z	R ²
C ₂ H ₅	Br	CH ₃	CH ₃
C ₂ H ₅	Br	CH ₃	C ₂ H ₅
C ₂ H ₅	Br	CH ₃	C ₃ H ₇
C ₂ H ₅	Br	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Br	CH ₃	C ₄ H ₉
C ₂ H ₅	Br	СН3	i-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -C ₆ H ₅
C ₂ H ₅	Br	СН3	C ₆ H ₅

Table 18: A, X, M and R^2 are as given in Table 17 Y = Br, $Z = C_2H_5$

10 Table 19: A, X, M and R² are as given in Table 17

$$Y = CI, Z = CH_3$$

Table 20: A, X, M and R^2 are as given in Table 17 Y = Cl, $Z = C_2H_5$

$$A \xrightarrow{\text{O}} Z \xrightarrow{\text{II-c}} (I-c)$$

5 Table 21 $A = C_3H_7$ M = O

X	Y	Z	R ²
C ₂ H ₅	Br	CH ₃	CH ₃
C ₂ H ₅	Br	СН3	C ₂ H ₅
C ₂ H ₅	Br	СН3	C ₃ H ₇
C ₂ H ₅	Br	СН3	i-C ₃ H ₇
C ₂ H ₅	Br	СН3	C ₄ H ₉
C ₂ H ₅	Br	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Br	СН3	CH ₂ -t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -C ₆ H ₅
C ₂ H ₅	Br	CH ₃	C ₆ H ₅

Table 22: A, X, M and R^2 are as given in Table 21 Y = Br, $Z = C_2H_5$

Table 23: A, X, M and R^2 are as given in Table 21 Y = Cl, $Z = CH_3$

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Table 24: A, X, M and R^2 are as given in Table 21 Y = Cl, $Z = C_2H_5$

Table 25 $A = CH_3$ M = S

X	Y	Z	R ²
C ₂ H ₅	Br	CH ₃	CH ₃
C ₂ H ₅	Br	CH ₃	C ₂ H ₅
C ₂ H ₅	Br	CH ₃	С ₃ Н ₇
C ₂ H ₅	Br	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Br	CH ₃	C ₄ H ₉
C ₂ H ₅	Br	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -C ₆ H ₅
C ₂ H ₅	Br	CH ₃	C ₆ H ₅

Table 26: A, X, M and R^2 are as given in Table 25 Y = Br, Z = C_2H_5

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Table 27: A, X, M and R^2 are as given in Table 25 Y = Cl, Z = CH₃

10 Table 28: A, X, M and R² are as given in Table 25

$$Y = Cl$$
, $Z = C_2H_5$

 $\underline{\textbf{Table 29}} \qquad \quad A = C_2 H_5 \qquad \quad M = S$

X	Y	Z	R ²
C ₂ H ₅	Br	CH ₃	CH ₃
C ₂ H ₅	Br	CH ₃	C ₂ H ₅
C ₂ H ₅	Br	CH ₃	C ₃ H ₇
C ₂ H ₅	Br	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Br	СН3	C ₄ H ₉
C ₂ H ₅	Br	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -C ₆ H ₅
C ₂ H ₅	Br	CH ₃	C ₆ H ₅

5 Table 30: A, X, M and R^2 are as given in Table 29 Y = Br, $Z = C_2H_5$

Table 31: A, X, M and R^2 are as given in Table 29 Y = Cl, Z = CH₃

Table 32: A, X, M and R^2 are as given in Table 29 Y = Cl, Z = C_2H_5

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$$A \xrightarrow{\text{O}} Z \xrightarrow{\text{II-c}} (I-c)$$

 $\underline{\textbf{Table 33}} \qquad \qquad A = C_3H_7 \qquad M = S$

X	Y	Z	R ²
C ₂ H ₅	Br	CH ₃	CH ₃
C ₂ H ₅	Br	CH ₃	C ₂ H ₅
C ₂ H ₅	Br	CH ₃	C ₃ H ₇
C ₂ H ₅	Br	CH ₃	i-C ₃ H ₇
C ₂ H ₅	Br	CH ₃	C ₄ H ₉
C ₂ H ₅	Br	CH ₃	i-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	s-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -t-C ₄ H ₉
C ₂ H ₅	Br	CH ₃	CH ₂ -C ₆ H ₅
C ₂ H ₅	Br	CH ₃	C ₆ H ₅

Table 34: A, X, M and R^2 are as given in Table 33 Y = Br, $Z = C_2H_5$

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<u>Table 35:</u> A, X, M and R^2 are as given in Table 33 Y = Cl, Z = CH₃

<u>Table 36:</u> A, X, M and R^2 are as given in Table 33 Y = Cl, Z = C_2H_5 Preferred meanings of the groups listed above in connection with the crop plant compatibility-improving compounds ("herbicide safeners") of the formulae (IIa), (IIb), (IIc), (IId) and (IIe) are defined below.

- m preferably represents the number 0, 1, 2, 3 or 4,
- 5 A¹ preferably represents one of the divalent heterocyclic groupings shown below

- n preferably represents the number 0, 1, 2, 3 or 4,
- A² preferably represents in each case optionally methyl-, ethyl-, methoxycarbonyl- or ethoxycarbonyl-substituted methylene or ethylene,
 - R¹² preferably represents hydroxyl, mercapto, amino, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino or diethylamino,
- preferably represents hydroxyl, mercapto, amino, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, 1-methylhexyloxy, allyloxy, 1-allyloxymethylethoxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino or diethylamino,
- R¹⁴ preferably represents in each case optionally fluorine-, chlorine- and/or bromine-20 substituted methyl, ethyl, n- or i-propyl,
 - preferably represents hydrogen, in each case optionally fluorine- and/or chlorinesubstituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, propenyl, butenyl, propynyl or butynyl, methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, dioxolanylmethyl,

furyl, furylmethyl, thienyl, thiazolyl, piperidinyl, or optionally fluorine-, chlorine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-substituted phenyl,

- R^{16} preferably represents hydrogen, in each case optionally fluorine- and/or chlorinesubstituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, propenyl, butenyl, propynyl 5 or butynyl, methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, dioxolanylmethyl, furyl, furylmethyl, thienyl, thiazolyl, piperidinyl, or optionally fluorine-, chlorine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-substituted phenyl, or together with $R^{15}\,$ -CH₂-O-CH₂-CH₂of radicals and one the represents -CH₂-CH₂-O-CH₂-CH₂- which are optionally substituted by methyl, ethyl, furyl, phenyl, a fused benzene ring or by two substituents which, together with the C atom 10 to which they are attached, form a 5- or 6-membered carbocycle,
 - R¹⁷ preferably represents hydrogen, cyano, fluorine, chlorine, bromine, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted methyl, ethyl, n- or i-propyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or phenyl,
- preferably represents hydrogen, optionally hydroxyl-, cyano-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl,
 - R¹⁹ preferably represents hydrogen, cyano, fluorine, chlorine, bromine, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or phenyl,
 - X¹ preferably represents nitro, cyano, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chlorodifluoromethyl, fluorodichloromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy,
- preferably represents hydrogen, nitro, cyano, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chlorodifluoromethyl, fluorodichloromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy,

- X³ preferably represents hydrogen, nitro, cyano, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chlorodifluoromethyl, fluorodichloromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy,
- 5 t preferably represents the number 0, 1, 2, 3 or 4,
 - v preferably represents the number 0, 1, 2, 3 or 4,
 - R²⁰ preferably represents hydrogen, methyl, ethyl, n- or i-propyl,
 - R²¹ preferably represents hydrogen, methyl, ethyl, n- or i-propyl,
- R^{22} preferably represents hydrogen, in each case optionally cyano-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or 10 t-butyl, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, methylthio, ethylthio, nor i-propylthio, n-, i-, s- or t-butylthio, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino or diethylamino, or in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl, cyclopentyloxy, cyclopentyloxy, cyclopentyloxy, 15 cyclopropylthio, cyclobutylthio, cyclopentylthio, cyclohexylthio, cyclohexyloxy, cyclopropylamino, cyclobutylamino, cyclopentylamino or cyclohexylamino,
- R²³ preferably represents hydrogen, in each case optionally cyano-, hydroxyl-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-,
 i- or s-butyl, in each case optionally cyano-, fluorine-, chlorine- or bromine-substituted propenyl, butenyl, propynyl or butynyl, or in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl,
- R²⁴ preferably represents hydrogen, in each case optionally cyano-, hydroxyl-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i- or s-butyl, in each case optionally cyano-, fluorine-, chlorine- or bromine-substituted propenyl, butenyl, propynyl or butynyl, in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, or optionally nitro-, cyano-, fluorine-, chlorine-, bromine-,

methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy- or trifluoromethoxy-substituted phenyl, or together with R²³ represents in each case optionally methyl- or ethyl-substituted butane-1,4-diyl (trimethylene), pentane-1,5-diyl, 1-oxabutane-1,4-diyl or 3-oxapentane-1,5-diyl,

5 X⁴ preferably represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, trifluoromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy,

x⁵ preferably represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, trifluoromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy.

Examples of the compounds of the formula (IIa) which are very particularly preferred as herbicide safeners according to the invention are listed in Table A below.

Table A: Examples of the compounds of the formula (IIa)

$$(X^1)_{m} \xrightarrow{4} \overset{3}{\downarrow} \overset{2}{\downarrow} \overset{O}{\downarrow} \overset{O}{\downarrow}$$
 (IIa)

Example No.	(positions) (X¹) _m	A ¹	R ¹²
IIa-1	(2) Cl, (4) Cl	H ₃ C OCH ₃	OCH₃
IIa-2	(2) Cl, (4) Cl	H ₃ C OC ₂ H ₅	OCH ₃

Example No.	(positions) (X ¹) _m	A ¹	R ¹²
IIa-3	(2) Cl, (4) Cl	H ₃ C OCH ₃	OC ₂ H ₅
IIa-4	(2) Cl, (4) Cl	H ₃ C OC ₂ H ₅	OC ₂ H ₅
IIa-5	(2) Cl	N N	OCH₃
IIa-6	(2) Cl, (4) Cl	N N	OCH₃
IIa-7	(2) F	N N	OCH ₃
Па-8	(2) F	N N CI	OCH₃

Example No.	(positions) (X¹) _m	A ¹	R ¹²
Па-9	(2) Cl, (4) Cl	Cl ₃ C	OC₂H₅
Ha-10	(2) Cl, (4) CF ₃	N N N	ОСН₃
Ha-11	(2) Cl	N N F	OCH ₃
IIa-12	-	O-N	OC ₂ H ₅
Па-13	(2) Cl, (4) Cl	H ₃ C	OC₂H₅
Ha-14	(2) Cl, (4) Cl	C ₃ H ₇ -i	OC ₂ H ₅
IIa-15	(2) Cl, (4) Cl	C ₄ H ₉ -t	OC ₂ H ₅
Па-16	(2) Cl, (4) Cl	H ₂ -C O-N	OC ₂ H ₅

Example No.	(positions) (X¹) _m	A^1	R ¹²
IIa-17	(2) Cl, (4) Cl	0-N	OC₂H₅
Па-18	-		ОН

Examples of the compounds of the formula (IIb) which are very particularly preferred as herbicide safeners according to the invention are listed in Table B below.

$$X^{3} \xrightarrow{5} X^{2}$$

$$X^{4} \xrightarrow{5} X^{2}$$

$$X^{5} \xrightarrow{5} X^{5}$$

$$X^{5} \xrightarrow{5}$$

Table B: Examples of the compounds of the formula (IIb)

5

Example No.	(position) X ²	(position) X ³	A ²	R ¹³
IIb-1	(5)	-	CH ₂	ОН
	Cl			
IIb-2	(5)	-	CH ₂	OCH ₃
	Cl			
IIb-3	(5)	-	CH ₂	OC ₂ H ₅
	Cl			
IIb-4	(5)	-	CH ₂	OC ₃ H ₇ -n
	Cl			ı

Example No.	(position) X ²	(position) X ³	A ²	R ¹³
IIb-5	(5)	_	CH ₂	OC ₃ H ₇ -i
	Cl			
	(2)		- Corr	0.0.11
IIb-6	(5)	-	CH ₂	OC₄H9-n
	Cl			
IIb-7	(5)	_	CH ₂	OCH(CH ₃)C ₅ H ₁₁ -n
	Cl			
IIb-8	(5)	(2)	CH ₂	ОН
	Cl	F		
TH. O	(5)	(2)	CH	ОН
IIb-9	(5)	(2)	CH ₂	OH
	Cl	Cl		
IIb-10	(5)		CH ₂	OCH ₂ CH=CH ₂
	Cl			
IIb-11	(5)	-	CH ₂	OC ₄ H ₉ -i
	Cl			
IIb-12	(5)	<u> </u>	CH ₂	CH ₂
110-12	Cl		0222	L CH
				H ₂ C C O H CH ₃
				O'H'CH ₃
IIb-13	(5)	-	CH ₂ II CH	OCH ₂ CH=CH ₂
	Cl		H ₂ C	
			, c.	
			/ Ă \	
			_L	

Example No.	(position) X ²	(position) X ³	A ²	R ¹³
IIb-14	(5) Cl	-	C ₂ H ₅ O O	OC₂H₅
Пb-15	(5) Cl	-	CH ₃	OCH ₃

Examples of the compounds of the formula (IIc) which are very particularly preferred as herbicide safeners according to the invention are listed in Table C below.

$$\mathbb{R}^{14} \longrightarrow \mathbb{N} \mathbb{R}^{15}$$

$$\mathbb{R}^{16}$$
(IIc)

Table C: Examples of the compounds of the formula (IIc)

5

Example No.	R ¹⁴	N(R ¹⁵ ,R ¹⁶)
IIc-1	CHCl ₂	N(CH ₂ CH=CH ₂) ₂
Пс-2	CHCl ₂	H ₃ C CH ₃
IIc-3	CHCl₂	H ₃ C CH ₃ O CH ₃

Example No.	R ¹⁴	N(R ¹⁵ ,R ¹⁶)
IIc-4	CHCl ₂	
IIc-5	CHCl ₂	H ₃ C CH ₃ O C ₆ H ₅
IIc-6	CHCl ₂	CH ₃
IIc-7	CHCl₂	H ₃ C CH ₃

Examples of the compounds of the formula (IId) which are very particularly preferred as herbicide safeners according to the invention are listed in Table D below.

$$O \bigvee_{R^{22}}^{R^{21}} \bigvee_{SO_2}^{(X^5)_v} \bigvee_{O}^{R^{20}} (X^4)_t$$
(IId)

5 Table D: Examples of the compounds of the formula (IId)

Example No.	\mathbb{R}^{20}	R ²¹	R ²²	(positions) (X ⁴) _t	(positions) (X ⁵) _v
IId-1	Н	Н	CH ₃	(2) OCH ₃	-
IId-2	H	Н	C ₂ H ₅	(2) OCH ₃	-
IId-3	Н	Н	C ₃ H ₇ -n	(2) OCH ₃	-
IId-4	H	Н	C ₃ H ₇ -i	(2) OCH ₃	-
IId-5	Н	Н		(2) OCH ₃	-
IId-6	H	Н	CH ₃	(2) OCH ₃ (5) CH ₃	-
IId-7	H	Н	C ₂ H ₅	(2) OCH ₃ (5) CH ₃	-
IId-8	H	Н	C ₃ H ₇ -n	(2) OCH ₃ (5) CH ₃	-
IId-9	Н	Н	C ₃ H ₇ -i	(2) OCH ₃ (5) CH ₃	-
IId-10	Н	Н		(2) OCH ₃ (5) CH ₃	-
IId-11	Н	Н	OCH₃	(2) OCH ₃ (5) CH ₃	-

Example No.	R ²⁰	\mathbb{R}^{21}	R ²²	(positions) (X ⁴)t	(positions) (X ⁵) _v
IId-12	Н	Н	OC ₂ H ₅	(2) OCH ₃	-
			-	(5) CH ₃	
IId-13	Н	Н	OC ₃ H ₇ -i	(2) OCH ₃	-
				(5) CH ₃	
IId-14	Н	Н	SCH ₃	(2) OCH ₃	-
				(5) CH ₃	
IId-15	Н	Н	SC ₂ H ₅	(2) OCH ₃	-
				(5) CH ₃	
IId-16	Н	Н	SC ₃ H ₇ -i	(2) OCH ₃	-
				(5) CH ₃	
IId-17	н	Н	NHCH₃	(2) OCH ₃	-
				(5) CH ₃	
IId-18	Н	Н	NHC ₂ H ₅	(2) OCH ₃	-
				(5) CH ₃	
IId-19	Н	Н	NHC ₃ H ₇ -i	(2) OCH ₃	-
				(5) CH ₃	
IId-20	H	Н	ŅH	(2) OCH ₃	-
				(5) CH ₃	
IId-21	H	Н	NHCH ₃	(2) OCH ₃	-

Example No.	R ²⁰	R ²¹	R ²²	(positions) (X ⁴) _t	(positions) (X ⁵) _v
IId-22	Н	Н	NHC ₃ H ₇ -i	(2) OCH ₃	-
IId-23	H .	Н	N(CH ₃) ₂	(2) OCH ₃	-
IId-24	H	Н	N(CH ₃) ₂	(3) CH ₃	-
				(4) CH ₃	
IId-25	Н	Н	CH ₂ -O-CH ₃	(2) OCH ₃	-

Examples of the compounds of the formula (IIe) which are very particularly preferred as herbicide safeners according to the invention are listed in Table E below.

5 Table E: Examples of the compounds of the formula (IIe)

Example No.	R ²⁰	R ²³	R ²⁴	(positions) (X ⁴) _t	(positions) (X ⁵) _v
IIe-1	Н	Н	CH ₃	(2) OCH ₃	-
IIe-2	H	Н	C ₂ H ₅	(2) OCH ₃	-
IIe-3	Н	Н	C ₃ H ₇ -n	(2) OCH ₃	-
IIe-4	H	Н	C ₃ H ₇ -i	(2) OCH ₃	-
IIe-5	Н	Н		(2) OCH ₃	-

Example No.	R ²⁰	R ²³	R ²⁴	(positions) (X ⁴),	(positions) (X ⁵) _v
IIe-6	H	CH ₃	CH ₃	(2) OCH ₃	-
IIe-7	Н	Н	CH₃	(2) OCH ₃	-
				(5) CH ₃	
IIe-8	H	Н	C ₂ H ₅	(2) OCH ₃	-
				(5) CH ₃	
IIe-9	Н	Н	C ₃ H ₇ -n	(2) OCH ₃	-
				(5) CH ₃	
IIe-10	Н	Н	C ₃ H ₇ -i	(2) OCH ₃	-
				(5) CH ₃	
IIe-11	Н	Н		(2) OCH ₃	-
				(5) CH₃	
IIe-12	H	CH ₃	CH ₃	(2) OCH ₃	-
				(5) CH ₃	

Most preferred as crop plant compatibility-improving compounds [component (b')] are cloquintocet-mexyl, fenchlorazole-ethyl, isoxadifen-ethyl, mefenpyr-diethyl, furilazole, fenclorim, cumyluron, dymron, dimepiperate and the compounds IIe-5 and IIe-11, and particular emphasis is given to cloquintocet-mexyl and mefenpyr-diethyl.

Examples of the selective herbicidal combinations according to the invention comprising in each case one active compound of the formulae (I-a) to (I-g) and in each case one of the safeners defined above are listed in Table F below.

<u>Table F:</u> Examples of the combinations according to the invention

Active compounds of the formula (I)	Safeners	
I-a	cloquintocet-mexyl	
I-a	fenchlorazole-ethyl	
I-a	isoxadifen-ethyl	
I-a	mefenpyr-diethyl	
I-a	furilazole	
I-a	fenclorim	
I-a	cumyluron	
I-a	daimuron /dymron	
I-a	dimepiperate	
I-a	IIe-11	
I-a	IIe-5	
I-b	cloquintocet-mexyl	
I-b	fenchlorazole-ethyl	
I-b	isoxadifen-ethyl	
I-b	mefenpyr-diethyl	
I-b	furilazole	
I-b	fenclorim	
I-b	cumyluron	
I-b	daimuron /dymron	
I-b	dimepiperate	
I-b	IIe-11	
I-b	Пе-5	
I-c	cloquintocet-mexyl	
I-c	fenchlorazole-ethyl	
I-c	isoxadifen-ethyl	
I-c	mefenpyr-diethyl	
I-c	furilazole	
I-c	fenclorim	
I-c	cumyluron	

	•
Active compounds of the formula (I)	Safeners
I-c	daimuron /dymron
I-c	dimepiperate
I-c	IIe-5
I-c	Пе-11
I-d	cloquintocet-mexyl
I-d	fenchlorazole-ethyl
I-d	isoxadifen-ethyl
I-d	mefenpyr-diethyl
I-d	furilazole
I-d	fenclorim
I-d	cumyluron
I-d	daimuron /dymron
I-d	dimepiperate
I-d	∐e-11
I-d	IIe-5
I-e	cloquintocet-mexyl
I-e	fenchlorazole-ethyl
I-e	isoxadifen-ethyl
I-e	mefenpyr-diethyl
I-e	furilazole
I-e	fenclorim
I-e	cumyluron
I-e	daimuron /dymron
I-e	dimepiperate
I-e	Пе-11
I-e	Пе-5
I-f	cloquintocet-mexyl
I-f	fenchlorazole-ethyl
I-f	isoxadifen-ethyl
I-f	mefenpyr-diethyl
I-f	furilazole
	<u></u>

Active compounds of the formula (I)	Safeners	
I-f	fenclorim	
I-f	cumyluron	
I-f	daimuron /dymron	
I-f	dimepiperate	
I-f	IIe-5	
I-f	Пе-11	
I-g	cloquintocet-mexyl	
I-g	fenchlorazole-ethyl	
I-g	isoxadifen-ethyl	
I-g	mefenpyr-diethyl	
I-g	furilazole	
I-g	fenclorim	
I-g	cumyluron	
I-g	daimuron /dymron	
I-g	dimepiperate	
I-g	Пе-5	
I-g	Пе-11	

The compounds of the general formula (IIa) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. WO-A-91/07874, WO-A-95/07897).

The compounds of the general formula (IIb) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. EP-A-191736).

The compounds of the general formula (IIc) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. DE-A-2218097, DE-A-2350547).

The compounds of the general formula (IId) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. DE-A-19621522/US-A-6235680).

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The compounds of the general formula (IIe) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. WO-A-99/66795/US-A-6251827).

Surprisingly, it has now been found that the active compound combinations defined above of substituted ketoenols of the general formula (I) and safeners (antidotes) from the component (b') listed above, while having very good compatibility with useful plants, have a particularly high herbicidal activity and can be used in various crops, in particular in cereals (especially wheat), but also in soya beans, potatoes, maize and rice, for the selective control of weeds.

Here, it has to be considered to be surprising that, from a large number of known safeners or antidotes capable of antagonizing the damaging effect of a herbicide on the crop plants, it is in particular the compounds of component (b') listed above which are suitable for compensating the damaging effect of substituted cyclic ketoenols on the crop plants almost completely, without negatively affecting the herbicidal activity against the weeds to any considerable extent.

Emphasis may be given here to the particularly advantageous effect of the particularly preferred and most preferred combination partners made from component (b'), in particular with respect to sparing cereal plants, such as, for example, wheat, barley and rye, but also maize and rice, as crop plants.

Using, for example, according to process (A) ethyl N-[(4-chloro-2,6-diethylphenyl)acetyl]1-amino-4-methoxycyclohexane-1-carboxylate as starting material, the course of the
process according to the invention can be represented by the reaction scheme below:

Using, for example, according to process (Bα) 8-methoxy-3-(4-chloro-2,6-diethyl-1-25 phenyl)-1-azaspiro[4,5]decane-2,4-dione and pivaloyl chloride as starting materials, the

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course of the process according to the invention can be represented by the reaction scheme below:

$$H_3CO$$
 H_5C_2
 CH_3
 CH_3

Using, for example, according to process (B), (variant B), 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and acetic anhydride as starting materials, the course of the process according to the invention can be represented by the reaction scheme below:

$$C_2H_5$$
 C_2H_5
 C_2H_5

Using, for example, according to process (C) 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and ethoxyethyl chloroformate as starting materials, the course of the process according to the invention can be represented by the reaction scheme below:

$$H_{3}CO$$

$$H_{5}C_{2}$$

$$C_{2}H_{5}$$

Using, for example, according to process (D), variant (α), 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and methyl chloromonothioformate as starting materials, the course of the reaction can be represented as follows:

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$$C_2H_5$$
 C_2H_5
 C_2H_5

Using, for example, according to process (D), variant (B), 8-methoxy-3-(4-bromo-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione, carbon disulphide and methyl iodide as starting materials, the course of the reaction can be represented as follows:

Br
$$C_2H_5$$
 OH OCH₃ $+CS_2$ $+CH_3I$ $+base$ C_2H_5 ONH OCH₃

Using, for example, according to process (E) 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and methanesulphonyl chloride as starting materials, the course of the reaction can be represented by the reaction scheme below:

$$H_3CO$$

OH

 C_2H_5
 C_2H_5

Using, for example, according to process (F) 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and 2,2,2-trifluoroethyl methanethiophosphonyl chloride as starting materials, the course of the reaction can be represented by the reaction scheme below:

$$H_3$$
CO

OH

 C_2H_5
 C_1
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5

Using, for example, according to process (G) 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and NaOH as components, the course of the reaction can be represented by the reaction scheme below:

$$H_3$$
CO

OH

 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5

Using, for example, according to process (H), variant (α), 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and ethyl isocyanate as starting materials, the course of the reaction can be represented by the reaction scheme below:

$$H_3$$
CO

 C_2H_5
 C_2H_5

Using, for example, according to process (H), variant (B), 8-methoxy-3-(4-chloro-2,6-diethylphenyl)-1-azaspiro[4,5]decane-2,4-dione and dimethylcarbamoyl chloride as starting materials, the course of the reaction can be represented by the scheme below:

$$H_3$$
CO

OH

 C_2H_5
 CI
 N
 CH_3
 CH_3
 CI
 CH_3
 CH_3
 CI
 CI
 CH_3
 CI
 CI

The compounds, required as starting materials in the process (a) according to the invention, of the formula (Π)

$$AO \longrightarrow CO_2R^8 Z$$
 (II)

in which

A, X, Y, Z and R^8 are as defined above

5 are novel.

The acylamino acid esters of the formula (II) are obtained, for example, when amino acid derivatives of the formula (XIV)

$$AO \longrightarrow CO_2R^8$$
 (XIV)

in which

10 A and R⁸ are as defined above

are acylated with substituted phenylacetic acid derivatives of the formula (XV)

$$Y \longrightarrow X$$
 Z
 COW
 Z
 Z

in which

X, Y and Z are as defined above and

15 W represents a leaving group introduced by carboxylic acid-activating reagents, such as carbonyldiimidazole, carbodiimides (such as, for example, dicyclohexylcarbodiimide), phosphorylating agents (such as, for example, POC₃,

BOP-Cl), halogenating agents, for example thionyl chloride, oxalyl chloride, phosgene or chloroformic esters

(Chem. Reviews 52, 237-416 (1953); Bhattacharya, Indian J. Chem. 6, 341-5, 1968) or when acylamino acids of the formula (XVI)

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

in which

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A, X, Y and Z are as defined above

are esterified (Chem. Ind. (London) 1568 (1968)).

The compounds of the formula (XVI)

$$\begin{array}{c|c}
 & X \\
 & Y \\
 & CO_2H & Z
\end{array}$$
(XVI)

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in which

A, X, Y and Z are as defined above

are novel.

The compounds of the formula (XVI) are obtained when amino acids of the formula (XVII)

$$NH_2$$
 CO_2H
(XVII)

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in which

A is as defined above

are acylated with substituted phenylacetic acid derivatives of the formula (XV)

$$Y - \bigvee_{Z}^{X} cow$$
 (XV)

in which

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X, Y and Z are as defined above and

W is as defined above,

for example according to Schotten-Baumann (Organikum, VEB Deutscher Verlag der Wissenschaften, Berlin 1977, p. 505).

Some of the compounds of the formula (XV) are known (EP-A-835243) and some are not known. They can be prepared by processes known in principle and as shown in the examples (see, for example, Henecka, Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Vol. 8, pp. 467-469 (1952)).

The compounds of the formula (XV) are obtained, for example, when substituted phenylacetic acids of the formula (XVIII)

$$Y \xrightarrow{X} CO_2H$$
 (XVIII)

in which X, Y and Z are as defined above

are reacted with halogenating agents (for example thionyl chloride, thionyl bromide, oxalyl chloride, phospene, phosphorus trichloride, phosphorus tribromide or phosphorus pentachloride), phosphonylating agents (such as, for example, POCl₃, BOP-Cl), carbonyldiimidazole, carbodiimides (for example dicyclohexylcarbodiimide), if appropriate in the presence of a diluent (for example optionally chlorinated aliphatic or aromatic

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hydrocarbons, such as toluene or methylene chloride, or ethers, for example tetrahydrofuran, dioxane, methyl tert-butyl ether), at temperatures of from -20°C to 150°C, preferably from -10°C to 100°C.

Some of the compounds of the formula (XVIII) are known (EP-A-835243), or they can be prepared analogously to the processes described therein.

Some of the compounds of the formulae (XIV) and (XVII) are known, and/or they can be prepared by known processes (EP-A 1 309 562).

The acid halides of the formula (III), carboxylic anhydrides of the formula (IV), chloroformic esters or chloroformic thioesters of the formula (V), chloromonothioformic esters or chlorodithioformic esters of the formula (VI), alkyl halides of the formula (VII), sulphonyl chlorides of the formula (VIII), phosphorus compounds of the formula (IX) and metal hydroxides, metal alkoxides or amines of the formulae (X) and (XI), respectively, and isocyanates of the formula (XII) and carbamoyl chlorides of the formula (XIII) furthermore required as starting materials for carrying out the processes (B), (C), (D), (E), (F), (G) and (H) according to the invention are generally known compounds of organic or inorganic chemistry.

The process (A) is characterized in that compounds of the formula (II) in which A, X, Y, Z and R⁸ are as defined above are subjected to an intramolecular condensation in the presence of a diluent and in the presence of a base.

Suitable diluents for the process (A) according to the invention are all organic solvents which are inert towards the reactants. Preference is given to using hydrocarbons, such as toluene and xylene, furthermore ethers, such as dibutyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether and diglycol dimethyl ether, moreover polar solvents, such as dimethyl sulphoxide, sulpholane, dimethylformamide and N-methylpyrrolidone, and also alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol and tert-butanol.

Suitable bases (deprotonating agents) for carrying out the process (A) according to the invention are all customary proton acceptors. Preference is given to using alkali metal and alkaline earth metal oxides, hydroxides and carbonates, such as sodium hydroxide, potassium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate and calcium carbonate, which can also be used in the presence of phase-transfer catalysts, such as, for

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example, triethylbenzylammonium chloride, tetrabutylammonium bromide, Adogen 464 (= methyltrialkyl(C₈-C₁₀)ammonium chloride) or TDA 1 (= tris(methoxyethoxyethyl)amine). It is furthermore possible to use alkali metals, such as sodium or potassium. Also suitable are alkali metal and alkaline earth metal amides and hydrides, such as sodium amide, sodium hydride and calcium hydride, and additionally also alkali metal alkoxides, such as sodium methoxide, sodium ethoxide and potassium tert-butoxide.

When carrying out the process (A) according to the invention, the reaction temperature can be varied within a relatively wide range. In general, the process is carried out at temperatures between 0°C and 250°C, preferably between 50°C and 150°C. The process (A) according to the invention is generally carried out under atmospheric pressure.

When carrying out the process (A) according to the invention, the reaction component of the formula (II) and the deprotonating base are generally employed in equimolar to about doubly equimolar amounts. However, it is also possible to use a relatively large excess (up to 3 mol) of one component or the other.

The process (Bα) is characterized in that compounds of the formula (I-a) are in each case reacted with carbonyl halides of the formula (III), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder. Suitable diluents for the process (Bα) according to the invention are all solvents which are inert towards the acid halides. Preference is given to using hydrocarbons, such as benzine, benzene, toluene, xylene and tetralin, furthermore halogenated hydrocarbons, such as methylene chloride, chloroform, carbon tetrachloride, chlorobenzene and o-dichlorobenzene, moreover ketones, such as acetone and methyl isopropyl ketone, furthermore ethers, such as diethyl ether, tetrahydrofuran and dioxane, additionally carboxylic esters, such as ethyl acetate, and also strongly polar solvents, such as dimethyl sulphoxide and sulpholane. The hydrolytic stability of the acid halide permitting, the reaction can also be carried out in the presence of water.

Suitable acid binders for the reaction according to the process (Bα) according to the invention are all customary acid acceptors. Preference is given to using tertiary amines, such as triethylamine, pyridine, diazabicyclooctane (DABCO), diazabicycloundecene (DBU), diazabicyclononene (DBN), Hünig base and N,N-dimethylaniline, furthermore alkaline earth metal oxides, such as magnesium oxide and calcium oxide, moreover alkali metal and alkaline

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earth metal carbonates, such as sodium carbonate, potassium carbonate and calcium carbonate, and also alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide.

In the process (Bα) according to the invention, the reaction temperature can be varied within a relatively wide range. In general, the process is carried out at temperatures between -20°C and +150°C, preferably between 0°C and 100°C.

When carrying out the process $(B\alpha)$ according to the invention, the starting materials of the formula (I-a) and the carbonyl halide of the formula (III) are generally each employed in approximately equivalent amounts. However, it is also possible to use a relatively large excess (up to 5 mol) of the carbonyl halide. Work-up is carried out by customary methods.

The process (Bβ) is characterized in that compounds of the formula (I-a) are in each case reacted with carboxylic anhydrides of the formula (IV), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

Suitable diluents for the process $(B\beta)$ according to the invention are preferably those diluents which are also preferred when using acid halides. Furthermore, excess carboxylic anhydride may simultaneously act as diluent.

The acid binders which are added, if appropriate, in the process $(B\beta)$ are preferably those acid binders which are also preferred when using acid halides.

The reaction temperature in the process (B β) according to the invention may be varied within a relatively wide range. In general, the process is carried out at temperatures between -20°C and +150°C, preferably between 0°C and 100°C.

When carrying out the process $(B\beta)$ according to the invention, the starting materials of the formula (I-a) and the carboxylic anhydride of the formula (IV) are generally each employed in approximately equivalent amounts. However, it is also possible to use a relatively large excess (up to 5 mol) of the carboxylic anhydride. Work-up is carried out by customary methods.

In general, diluent and excess carboxylic anhydride and the carboxylic acid formed are removed by distillation or by washing with an organic solvent or with water.

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The process (C) is characterized in that compounds of the formula (I-a) are in each case reacted with chloroformic esters or chloroformic thioesters of the formula (V) if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

Suitable acid binders for the process (C) according to the invention are all customary acid acceptors. Preference is given to using tertiary amines, such as triethylamine, pyridine, DABCO, DBU, DBA, Hünig base and N,N-dimethylaniline, furthermore alkaline earth metal oxides, such as magnesium oxide and calcium oxide, moreover alkali metal and alkaline earth metal carbonates, such as sodium carbonate, potassium carbonate and calcium carbonate, and also alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide.

Suitable diluents for the process (C) according to the invention are all solvents which are inert towards the chloroformic esters or chloroformic thioesters. Preference is given to using hydrocarbons, such as benzine, benzene, toluene, xylene and tetralin, furthermore halogenated hydrocarbons, such as methylene chloride, chloroform, carbon tetrachloride, chlorobenzene and o-dichlorobenzene, moreover ketones, such as acetone and methyl isopropyl ketone, furthermore ethers, such as diethyl ether, tetrahydrofuran and dioxane, additionally carboxylic esters, such as ethyl acetate, and also strongly polar solvents, such as dimethyl sulphoxide and sulpholane.

When carrying out the process (C) according to the invention, the reaction temperature can be varied within a relatively wide range. In general, the reaction temperature is between -20°C and +100°C, preferably between 0°C and 50°C.

The process (C) according to the invention is generally carried out under atmospheric pressure. When carrying out the process (C) according to the invention, the starting materials of the formula (I-a) and the appropriate chloroformic ester or chloroformic thioester of the formula (V) are generally each employed in approximately equivalent amounts. However, it is also possible to use a relatively large excess (up to 2 mol) of one component or the other. Work-up is carried out by customary methods. In general, precipitated salts are removed and the reaction mixture which remains is concentrated by removing the diluent under reduced pressure.

The process (D) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with $(D\alpha)$ compounds of the formula (VI) in the presence of a diluent and, if appropriate, in the presence of an acid binder or $(D\beta)$ carbon disulphide and then with

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alkyl halides of the formula (VII), if appropriate in the presence of a diluent and if appropriate in the presence of a base.

In the preparation process (Dα), about 1 mol of chloromonothioformic ester or chlorodithioformic ester of the formula (VI) is reacted per mole of starting material of the formula (I-a), at from 0 to 120°C, preferably from 20 to 60°C.

Suitable diluents, which are added, if appropriate, are all inert polar organic solvents, such as ethers, esters, amides, sulphones, sulphoxides, but also halogenated alkanes.

Preference is given to using dimethyl sulphoxide, ethyl acetate, tetrahydrofuran, dimethylformamide or methylene chloride.

If, in a preferred embodiment, the enolate salt of the compound (I-a) is prepared by adding strong deprotonating agents, such as, for example, sodium hydride or potassium tert-butoxide, the further addition of acid binders may be dispensed with.

If acid binders are used, these are customary inorganic or organic bases, for example sodium hydroxide, sodium carbonate, potassium carbonate, pyridine and triethylamine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods.

In the preparation process (D β), in each case the equimolar amount or an excess of carbon disulphide is added per mole of starting material of the formula (I-a). The process is preferably carried out at temperatures of from 0 to 50°C and in particular at from 20 to 30°C.

Frequently, it is expedient to prepare initially the corresponding salt from the compounds of the formula (I-a) by adding a base (such as, for example, potassium tert-butoxide or sodium hydride). In each case, the compound (I-a) is reacted with carbon disulphide until the formation of the intermediate has ended, for example after several hours of stirring at room temperature.

Suitable bases for the process (D\(\beta\)) are all customary proton acceptors. Preference is given to using alkali metal hydrides, alkali metal alkoxides, alkali metal or alkaline earth metal carbonates or bicarbonates or nitrogen bases. Examples which may be mentioned are sodium hydride, sodium methoxide, sodium hydroxide, calcium hydroxide, potassium carbonate, sodium

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bicarbonate, triethylamine, dibenzylamine, diisopropylethylamine, pyridine, quinoline, diazabicyclooctane (DABCO), diazabicyclononene (DBN) and diazabicycloundecene (DBU).

Suitable diluents are all solvents which are customary for this process.

Preference is given to using aromatic hydrocarbons, such as benzene or toluene, alcohols, such as methanol, ethanol, isopropanol or ethylene glycol, nitriles, such as acetonitrile, ethers, such as tetrahydrofuran or dioxane, amides, such as dimethylformamide, or other polar solvents, such as dimethyl sulphoxide or sulpholane.

The further reaction with the alkyl halide of the formula (VII) is preferably carried out at from 0 to 70°C and in particular at from 20 to 50°C. Here, at least the equimolar amount of alkyl halide is used.

The process is carried out at atmospheric pressure or under elevated pressure, preferably at atmospheric pressure.

Work-up is again carried out by customary methods.

The process (E) according to the invention is characterized in that compounds of the formula (Ia) are in each case reacted with sulphonyl chlorides of the formula (VIII), if appropriate in the
presence of a diluent and if appropriate in the presence of an acid binder.

In the preparation process (E), about 1 mol of sulphonyl chloride of the formula (VIII) is reacted per mole of starting material of the formula (I-a), at from -20 to 150°C, preferably from 20 to 70°C.

The process (E) is preferably carried out in the presence of a diluent. Suitable diluents are all inert polar organic solvents, such as ethers, esters, amides, nitriles, sulphones, sulphoxides or halogenated hydrocarbons, such as methylene chloride.

Preference is given to using dimethyl sulphoxide, tetrahydrofuran, ethyl acetate, dimethylformamide, methylene chloride.

If, in a preferred embodiment, the enolate salt of the compound (I-a) or (I-a') is prepared by adding strong deprotonating agents (such as, for example, sodium hydride or potassium tert-butoxide), the further addition of acid binders may be dispensed with.

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If acid binders are used, these are customary inorganic or organic bases, for example sodium hydroxide, sodium carbonate, potassium carbonate, pyridine and triethylamine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods.

The process (F) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with phosphorus compounds of the formula (IX), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

In the preparation process (F), to obtain compounds of the formula (I-e), 1 to 2, preferably 1 to 1.3, mol of the phosphorus compound of the formula (IX) are reacted per mole of the compound (I-a), at temperatures between -40°C and 150°C, preferably between -10 and 110°C.

The process (F) is preferably carried out in the presence of a diluent. Suitable diluents are all inert polar organic solvents, such as ethers, esters, amides, nitriles, sulphides, sulphones, sulphoxides, etc.

Preference is given to using acetonitrile, ethyl acetate, dimethyl sulphoxide, tetrahydrofuran, dimethylformamide, methylene chloride.

Suitable acid binders, which are added if appropriate, are customary inorganic or organic bases, such as hydroxides, carbonates or amines. Examples which may be mentioned are sodium hydroxide, sodium carbonate, potassium carbonate, pyridine and triethylamine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods of organic chemistry. The end products are preferably purified by crystallization, chromatographic purification or by "incipient distillation", i.e. removal of the volatile components under reduced pressure.

The process (G) is characterized in that compounds of the formula (I-a) are in each case reacted with metal hydroxides or metal alkoxides of the formula (X) or amines of the formula (XI), if appropriate in the presence of a diluent.

Suitable diluents for the process (G) according to the invention are preferably ethers, such as tetrahydrofuran, dioxane, diethyl ether or else alcohols, such as methanol, ethanol, isopropanol,

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but also water. The process (G) according to the invention is generally carried out under atmospheric pressure. The reaction temperature is generally between -20°C and 100°C, preferably between 0°C and 50°C.

The process (H) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with (H α) compounds of the formula (XII), if appropriate in the presence of a diluent and if appropriate in the presence of a catalyst, or (H β) with compounds of the formula (XIII), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

In preparation process (Ha), about 1 mol of isocyanate of the formula (XII) is reacted per mole of starting material of the formula (I-a), at from 0 to 100°C, preferably at from 20 to 50°C.

The process (Ha) is preferably carried out in the presence of a diluent.

Suitable diluents are all inert organic solvents, such as ethers, esters, amides, nitriles, sulphones or sulphoxides.

If appropriate, catalysts may be added to accelerate the reaction. Suitable for use as catalysts are, very advantageously, organotin compounds, such as, dibutyltin dilaurate.

The process is preferably carried out at atmospheric pressure.

In the preparation process (H β), about 1 mol of carbamoyl chloride of the formula (XIII) is reacted per mole of starting material of the formula (I-a), at from 0 to 150°C, preferably at from 20 to 70°C.

Suitable diluents which are added, if appropriate, are all inert polar organic solvents, such as ethers, esters, amides, sulphones, sulphoxides or halogenated hydrocarbons.

Preference is given to using dimethyl sulphoxide, ethyl acetate, tetrahydrofuran, dimethylformamide or methylene chloride.

If, in a preferred embodiment, the enolate salt of the compound (I-a) is prepared by adding strong deprotonating agents (such as, for example, sodium hydride or potassium tert-butoxide), the further addition of acid binders may be dispensed with.

If acid binders are used, these are customary inorganic or organic bases, for example sodium hydroxide, sodium carbonate, potassium carbonate, triethylamine or pyridine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods.

The active compounds are well tolerated by plants and have advantageous toxicity to warm-blooded species; they can be employed for controlling animal pests, in particular insects, arachnids and nematodes encountered in agriculture, forests, in the protection of stored products and materials and in the hygiene sector. They may preferably be used as crop protection agents. They are active against normally sensitive and resistant species and against all or some stages of development. The abovementioned pests include:

From the order of the Isopoda, for example, Oniscus asellus, Armadillidium vulgare and Porcellio scaber.

From the order of the Diplopoda, for example, Blaniulus guttulatus.

From the order of the Chilopoda, for example, Geophilus carpophagus and Scutigera spp.

15 From the order of the Symphyla, for example, Scutigerella immaculata.

From the order of the Thysanura, for example, Lepisma saccharina.

From the order of the Collembola, for example, Onychiurus armatus.

From the order of the Orthoptera, for example, Acheta domesticus, Gryllotalpa spp., Locusta migratoria migratorioides, Melanoplus spp. and Schistocerca gregaria.

From the order of the Blattaria, for example, Blatta orientalis, Periplaneta americana, Leucophaea maderae and Blattella germanica.

From the order of the Dermaptera, for example, Forficula auricularia.

From the order of the Isoptera, for example, Reticulitermes spp.

From the order of the Phthiraptera, for example, Pediculus humanus corporis, Haematopinus spp., Linognathus spp., Trichodectes spp., Damalinia spp.

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From the order of the Thysanoptera, for example, Hercinothrips femoralis, Thrips tabaci, Thrips palmi, Frankliniella accidentalis.

From the order of the Heteroptera, for example, Eurygaster spp., Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus and Triatoma spp.

From the order of the Homoptera, for example, Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus ribis, Aphis fabae, Aphis pomi, Eriosoma lanigerum, Hyalopterus arundinis, Phylloxera vastatrix, Pemphigus spp., Macrosiphum avenae, Myzus spp., Phorodon humuli, Rhopalosiphum padi, Empoasca spp., Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens, Aonidiella aurantii, Aspidiotus hederae, Pseudococcus spp. and Psylla spp.

From the order of the Lepidoptera, for example, Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponomeuta padella, Plutella xylostella, Malacosoma neustria, Euproctis chrysorrhoea, Lymantria spp., Bucculatrix thurberiella, Phyllocnistis citrella, Agrotis spp., Euxoa spp., Feltia spp., Earias insulana, Heliothis spp., Mamestra brassicae, Panolis flammea, Spodoptera spp., Trichoplusia ni, Carpocapsa pomonella, Pieris spp., Chilo spp., Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Tineola bisselliella, Tinea pellionella, Hofmannophila pseudospretella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiguella, Homona magnanima, Tortrix viridana, Cnaphalocerus spp. and Oulema oryzae.

From the order of the Coleoptera, for example, Anobium punctatum, Rhizopertha dominica, Bruchidius obtectus, Acanthoscelides obtectus, Hylotrupes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp., Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus surinamensis, Anthonomus spp., Sitophilus spp., Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes spp., Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus, Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solstitialis, Costelytra zealandica and Lissorphoptrus oryzophilus.

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From the order of the Hymenoptera, for example, Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis and Vespa spp.

From the order of the Diptera, for example, Aedes spp., Anopheles spp., Culex spp., Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala, Lucilia spp., Chrysomyia spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae, Tipula paludosa, Hylemyia spp. and Liriomyza spp.

From the order of the Siphonaptera, for example, Xenopsylla cheopis and Ceratophyllus spp.

From the class of the Arachnida, for example, Scorpio maurus, Latrodectus mactans, Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis, Phyllocoptruta oleivora, Boophilus spp., Rhipicephalus spp., Amblyomma spp., Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp., Tetranychus spp., Hemitarsonemus spp. and Brevipalpus spp.

The plant-parasitic nematodes include, for example, Pratylenchus spp., Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Globodera spp., Meloidogyne spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp., Trichodorus spp. and Bursaphelenchus spp.

If appropriate, the compounds or active compound combinations according to the invention may also be used in certain concentrations or application rates to act as herbicides. If appropriate, they can also be employed as intermediates or precursors for the synthesis of further active compounds.

All plants and plant parts can be treated in accordance with the invention. Plants are to be understood as meaning in the present context all plants and plant populations such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional plant breeding and optimization methods or by biotechnological and recombinant methods or by combinations of these methods, including the transgenic plants and inclusive of the plant cultivars protectable or not protectable by plant breeders' rights. Plant parts are to be understood as

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meaning all parts and organs of plants above and below the ground, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stalks, stems, flowers, fruit bodies, fruits and seeds and also roots, tubers and rhizomes. The plant parts also include harvested material, and vegetative and generative propagation material, for example cuttings, tubers, rhizomes, offsets and seeds.

The treatment according to the invention of the plants and plant parts with the active compounds or active compound combinations is carried out directly or by allowing the compounds to act on their surroundings, habitat or storage space by the customary treatment methods, for example by immersion, spraying, atomizing, evaporation, fogging, scattering or painting on and, in the case of propagation material, in particular in the case of seeds, also by applying one or more coats.

The active compounds or active compound combinations can be converted into the customary formulations such as solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble powders, granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with active compound, and microencapsulations in polymeric materials.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is, liquid solvents and/or solid carriers, optionally with the use of surfactants, that is, emulsifiers and/or dispersants and/or foam formers.

If the extender used is water, it is also possible, for example, to use organic solvents as cosolvents. The following are essentially suitable as liquid solvents: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, or else water.

Suitable solid carriers are:

for example ammonium salts and ground natural minerals such as kaolins, clays, talc, chalk,

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quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic materials such as highly disperse silica, alumina and silicates; suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, or else protein hydrolysates; suitable dispersants are: for example lignin-sulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic colorants such as alizarin colorants, azo colorants and metal phthalocyanine colorants, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention, as such or in their formulations, can also be used as a mixture with known fungicides, bactericides, acaricides, nematicides or insecticides, for example in order to widen the spectrum of action or to prevent the development of resistances in this way. In many cases, synergistic effects result, i.e. the activity of the mixture exceeds the activity of the individual components.

Compounds which are suitable as components in the mixtures are, for example, the following:

Fungicides:

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aldimorph, ampropylfos, ampropylfos-potassium, andoprim, anilazine, azaconazole, azoxystrobin,

benalaxyl, benodanil, benomyl, benzamacril, benzamacril-isobutyl, bialaphos, binapacryl, biphenyl, bitertanol, blasticidin-S, bromuconazole, bupirimate, buthiobate,

calcium polysulphide, capsimycin, captafol, captan, carbendazim, carboxin, carvon, quinomethionate, chlobenthiazone, chlorfenazole, chloroneb, chloropicrin, chlorothalonil, chlozolinate, clozylacon, cufraneb, cymoxanil, cyproconazole, cyprodinil, cyprofuram,

debacarb, dichlorophen, diclobutrazole, diclofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole, diniconazole-M, dinocap, diphenylamine, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, drazoxolon,

edifenphos, epoxiconazole, etaconazole, ethirimol, etridiazole,

famoxadon, fenapanil, fenarimol, fenbuconazole, fenfuram, fenitropan, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, flumetover, fluoromide, fluquinconazole, flurprimidol, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fosetyl-sodium, fthalide, fuberidazole, furalaxyl, furametpyr, furcarbonil, furconazole, furconazole-cis, furmecyclox,

guazatine,

hexachlorobenzene, hexaconazole, hymexazole,

imazalil, imibenconazole, iminoctadine, iminoctadine albesilate, iminoctadine triacetate, iodocarb, ipconazole, iprobenfos (IBP), iprodione, irumamycin, isoprothiolane, isovaledione,

kasugamycin, kresoxim-methyl, copper preparations, such as: copper hydroxide, copper naphthenate, copper oxychloride, copper sulphate, copper oxide, oxine-copper and Bordeaux mixture,

mancopper, mancozeb, maneb, meferimzone, mepanipyrim, mepronil, metalaxyl, metconazole, methasulfocarb, methfuroxam, metiram, metomeclam, metsulfovax,

mildiomycin, myclobutanil, myclozolin,

nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol,

ofurace, oxadixyl, oxamocarb, oxolinic acid, oxycarboxim, oxyfenthiin,

paclobutrazole, pefurazoate, penconazole, pencycuron, phosdiphen, picoxystrobin, pimaricin, piperalin, polyoxin, polyoxorim, probenazole, prochloraz, procymidone, propamocarb, propanosine-sodium, propiconazole, propineb, pyraclostrobin, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur,

quinconazole, quintozene (PCNB),

sulphur and sulphur preparations,

tebuconazole, tecloftalam, tecnazene, tetcyclacis, tetraconazole, thiabendazole, thicyofen, thifluzamide, thiophanate-methyl, thiram, tioxymid, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, trichlamide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole,

uniconazole,

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15 validamycin A, vinclozolin, viniconazole,

zarilamide, zineb, ziram and also

Dagger G,

OK-8705, OK-8801,

 α -(1,1-dimethylethyl)- β -(2-phenoxyethyl)-1H-1,2,4-triazole-1-ethanol,

20 α -(2,4-dichlorophenyl)- β -fluoro- β -propyl-1H-1,2,4-triazole-1-ethanol,

 α -(2,4-dichlorophenyl)- β -methoxy- α -methyl-1H-1,2,4-triazole-1-ethanol,

 α -(5-methyl-1,3-dioxan-5-yl)- β -[[4-(trifluoromethyl)phenyl]methylene]-1H-1,2,4-triazole-1-ethanol,

(5RS,6RS)-6-hydroxy-2,2,7,7-tetramethyl-5-(1H-1,2,4-triazol-1-yl)-3-octanone,

- (E)-α-(methoxyimino)-N-methyl-2-phenoxyphenylacetamide,
- 1-isopropyl {2-methyl-1-[[[1-(4-methylphenyl)ethyl]amino]carbonyl]propyl}carbamate,
- 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)ethanone O-(phenylmethyl)oxime,
- 1-(2-methyl-1-naphthalenyl)-1H-pyrrole-2,5-dione,
- 5 1-(3,5-dichlorophenyl)-3-(2-propenyl)-2,5-pyrrolidinedione,
 - 1-[(diiodomethyl)sulphonyl]-4-methylbenzene,
 - 1-[[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]methyl]-1H-imidazole,
 - 1-[[2-(4-chlorophenyl)-3-phenyloxiranyl]methyl]-1H-1,2,4-triazole,
 - 1-[1-[2-[(2,4-dichlorophenyl)methoxy]phenyl]ethenyl]-1H-imidazole,
- 10 1-methyl-5-nonyl-2-(phenylmethyl)-3-pyrrolidinol,
 - 2',6'-dibromo-2-methyl-4'-trifluoromethoxy-4'-trifluoromethyl-1,3-thiazole-5-carboxanilide,
 - 2,2-dichloro-N-[1-(4-chlorophenyl)ethyl]-1-ethyl-3-methylcyclopropanecarboxamide,
 - 2,6-dichloro-5-(methylthio)-4-pyrimidinyl thiocyanate,
- 15 2,6-dichloro-N-(4-trifluoromethylbenzyl)benzamide,
 - 2,6-dichloro-N-[[4-(trifluoromethyl)phenyl]methyl]benzamide,
 - 2-(2,3,3-triiodo-2-propenyl)-2H-tetrazole,
 - 2-[(1-methylethyl)sulphonyl]-5-(trichloromethyl)-1,3,4-thiadiazole,
- 2-[[6-deoxy-4-O-(4-O-methyl-β-D-glycopyranosyl)-α-D-glucopyranosyl]amino]-4-20 methoxy-1H-pyrrolo[2,3-d]pyrimidine-5-carbonitrile,
 - 2-aminobutane,
 - 2-bromo-2-(bromomethyl)pentanedinitrile,

- 2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridinecarboxamide,
- 2-chloro-N-(2,6-dimethylphenyl)-N-(isothiocyanatomethyl)acetamide,
- 2-phenylphenol (OPP),
- 3,4-dichloro-1-[4-(difluoromethoxy)phenyl]-1H-pyrrole-2,5-dione,
- 5 3,5-dichloro-N-[cyano-[(1-methyl-2-propynyl)oxy]methyl]benzamide,
 - 3-(1,1-dimethylpropyl)-1-oxo-1H-indene-2-carbonitrile,
 - 3-[2-(4-chlorophenyl)-5-ethoxy-3-isoxazolidinyl]pyridine,
 - 4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)-1H-imidazole-1-sulphonamide,
 - 4-methyltetrazolo[1,5-a]quinazolin-5(4H)-one,
- 8-(1,1-dimethylethyl)-N-ethyl-N-propyl-1,4-dioxaspiro[4.5]decane-2-methanamine,
 - 8-hydroxyquinoline sulphate,
 - 9H-xanthene-2-[(phenylamino)carbonyl]-9-carboxylic hydrazide,
 - bis-(1-methylethyl)-3-methyl-4-[(3-methylbenzoyl)oxy]-2,5-thiophene dicarboxylate,
 - cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)cycloheptanol,
- cis-4-[3-[4-(1,1-dimethylpropyl)phenyl-2-methylpropyl]-2,6-dimethylmorpholine hydrochloride,
 - ethyl [(4-chlorophenyl)azo]cyanoacetate,
 - potassium bicarbonate,
 - methanetetrathiol sodium salt,
- 20 methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate,
 - methyl N-(2,6-dimethylphenyl)-N-(5-isoxazolylcarbonyl)-DL-alaninate,
 - methyl N-(chloroacetyl)-N-(2,6-dimethylphenyl)-DL-alaninate,

N-(2,3-dichloro-4-hydroxyphenyl)-1-methylcyclohexanecarboxamide,

N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-furanyl)acetamide,

N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-thienyl)acetamide,

N-(2-chloro-4-nitrophenyl)-4-methyl-3-nitrobenzenesulphonamide,

5 N-(4-cyclohexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidinamine,

N-(4-hexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidinamine,

N-(5-chloro-2-methylphenyl)-2-methoxy-N-(2-oxo-3-oxazolidinyl)acetamide,

N-(6-methoxy)-3-pyridinylcyclopropanecarboxamide,

N-[2,2,2-trichloro-1-[(chloroacetyl)amino]ethyl]benzamide,

10 N-[3-chloro-4,5-bis(2-propinyloxy)phenyl]-N'-methoxymethanimidamide,

N-formyl-N-hydroxy-DL-alanine sodium salt,

O,O-diethyl [2-(dipropylamino)-2-oxoethyl]ethylphosphoramidothioate,

O-methyl S-phenyl phenylpropylphosphoramidothioate,

S-methyl 1,2,3-benzothiadiazole-7-carbothioate,

spiro[2H]-1-benzopyrane-2,1'(3'H)-isobenzofuran-3'-one,

4-[(3,4-dimethoxyphenyl)-3-(4-fluorophenyl)acryloyl]morpholine.

Bactericides:

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bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin, octhilinone, furancarboxylic acid, oxytetracyclin, probenazole, streptomycin, tecloftalam, copper sulphate and other copper preparations.

Insecticides/acaricides/nematicides:

abamectin, acephate, acetamiprid, acrinathrin, alanycarb, aldicarb, aldoxycarb, alphacypermethrin, alphamethrin, amitraz, avermectin, AZ 60541, azadirachtin, azamethiphos, azinphos A, azinphos M, azocyclotin,

Bacillus popilliae, Bacillus sphaericus, Bacillus subtilis, Bacillus thuringiensis, baculoviruses,
5 Beauveria bassiana, Beauveria tenella, bendiocarb, benfuracarb, bensultap, benzoximate,
betacyfluthrin, bifenazate, bifenthrin, bioethanomethrin, biopermethrin, bistrifluron, BPMC,
bromophos A, bufencarb, buprofezin, butathiofos, butocarboxim, butylpyridaben,

cadusafos, carbaryl, carbofuran, carbophenothion, carbosulfan, cartap, chloethocarb, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, chlorfluazuron, chlormephos, chlorpyrifos, chlorpyrifos M, chlovaporthrin, chromafenozide, cis-resmethrin, cispermethrin, clocythrin, cloethocarb, clofentezine, clothianidine, cyanophos, cycloprene, cycloprothrin, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyromazine,

deltamethrin, demeton M, demeton S, demeton-S-methyl, diafenthiuron, diazinon, dichlorvos, dicofol, diflubenzuron, dimethoate, dimethylvinphos, diofenolan, disulfoton, docusat-sodium, dofenapyn,

eflusilanate, emamectin, empenthrin, endosulfan, Entomopfthora spp., esfenvalerate, ethiofencarb, ethion, ethoprophos, etofenprox, etoxazole, etrimfos,

fenothiocarb, fenoxacrim, fenbutatin oxide, fenitrothion, fenamiphos, fenazaguin, fenoxycarb, fenpropathrin, fenpyrad, fenpyrithrin, fenpyroximate, fenvalerate, fipronil, flufenoxuron, flucythrinate, flucycloxuron, fluazinam, fluazuron, flubrocythrinate, fosmethilan, fosthiazate, fubfenprox, fluvalinate, fonophos, flutenzine, flumethrin, furathiocarb,

granulosis viruses,

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halofenozide, HCH, heptenophos, hexaflumuron, hexythiazox, hydroprene,

25 imidacloprid, indoxacarb, isazofos, isofenphos, isoxathion, ivermectin,

nuclear polyhedrosis viruses,

lambda-cyhalothrin, lufenuron,

Metharhizium anisopliae, metaldehyde, methamidophos, malathion, mecarbam, methomyl, flavoviride, methoprene, Metharhizium methidathion, methiocarb, metoxadiazone, mevinphos, milbemectin. milbemycin, methoxyfenozide. metolcarb, monocrotophos,

5 naled, nitenpyram, nithiazine, novaluron,

omethoate, oxamyl, oxydemethon M,

Paecilomyces fumosoroseus, parathion A, parathion M, permethrin, phenthoate, phorate, phosalone, phosmet, phosphamidon, phoxim, pirimicarb, pirimiphos A, pirimiphos M, profenofos, promecarb, propargite, propoxur, prothiofos, prothoate, pymetrozine, pyraclofos, pyresmethrin, pyrethrum, pyridaben, pyridathion, pyrimidifen, pyriproxyfen,

quinalphos,

ribavirin,

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salithion, sebufos, silafluofen, spinosad, spirodiclofen, sulfotep, sulprofos,

tau-fluvalinate, tebufenozide, tebufenpyrad, tebupirimiphos, teflubenzuron, tefluthrin, temephos, temivinphos, terbufos, tetrachlorvinphos, tetradifon, theta-cypermethrin, thiacloprid, thiamethoxam, thiapronil, thiatriphos, thiocyclam hydrogen oxalate, thiodicarb, thiofanox, thuringiensin, tralocythrin, tralomethrin, triarathene, triazamate, triazophos, triazurone, trichlophenidine, trichlorfon, triflumuron, trimethacarb,

vamidothion, vaniliprole, Verticillium lecanii,

20 YI 5302,

zeta-cypermethrin, zolaprofos

(1R-cis)-[5-(phenylmethyl)-3-furanyl]methyl 3-[(dihydro-2-oxo-3(2H)-furanylidene)methyl]-2,2-dimethylcyclopropanecarboxylate,

(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate,

25 1-[(2-chloro-5-thiazolyl)methyl]tetrahydro-3,5-dimethyl-N-nitro-1,3,5-triazine-2(1H)-imine,

- 2-(2-chloro-6-fluorophenyl)-4-[4-(1,1-dimethylethyl)phenyl]-4,5-dihydrooxazole,
- 2-(acetyloxy)-3-dodecyl-1,4-naphthalenedione,
- 2-chloro-N-[[[4-(1-phenylethoxy)phenyl]amino]carbonyl]benzamide,
- 2-chloro-N-[[[4-(2,2-dichloro-1,1-difluoroethoxy)phenyl]amino]carbonyl]benzamide,
- 5 3-methylphenyl propylcarbamate,
 - 4-[4-(4-ethoxyphenyl)-4-methylpentyl]-1-fluoro-2-phenoxybenzene,
 - 4-chloro-2-(1,1-dimethylethyl)-5-[[2-(2,6-dimethyl-4-phenoxyphenoxy)ethyl]thio]-3(2H)-pyridazinone,
- 4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)pyridazinone,
 - 4-chloro-5-[(6-chloro-3-pyridinyl)methoxy]-2-(3,4-dichlorophenyl)-3(2H)-pyridazinone, Bacillus thuringiensis strain EG-2348,
 - [2-benzoyl-1-(1,1-dimethylethyl)]hydrazinobenzoic acid,
 - 2,2-dimethyl-3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl butanoate,
- 15 [3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene]cyanamide,
 - dihydro-2-(nitromethylene)-2H-1,3-thiazine-3(4H)-carboxaldehyde,
 - ethyl [2-[[1,6-dihydro-6-oxo-1-(phenylmethyl)-4-pyridazinyl]oxy]ethyl]carbamate,
 - N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine,
- N-(4-chlorophenyl)-3-[4-(difluoromethoxy)phenyl]-4,5-dihydro-4-phenyl-1H-pyrazole-1-20 carboxamide,
 - N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitroguanidine,
 - N-methyl-N'-(1-methyl-2-propenyl)-1,2-hydrazinedicarbothioamide,

N-methyl-N'-2-propenyl-1,2-hydrazinedicarbothioamide,

O,O-diethyl [2-(dipropylamino)-2-oxoethyl]ethylphosphoramidothioate,

N-cyanomethyl-4-trifluoromethylnicotinamide,

3,5-dichloro-1-(3,3-dichloro-2-propenyloxy)-4-[3-(5-trifluoromethylpyridin-2-

5 yloxy)propoxy]benzene.

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A mixture with other known active compounds, such as herbicides, or with fertilizers and growth regulators, is also possible.

When used as insecticides in their commercially available formulations and in the use forms prepared with these formulations, the active compounds according to the invention can furthermore exist in the form of a mixture with synergists. Synergists are compounds by which the activity of the active compounds is increased without it being necessary for the synergist added to be active itself.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide ranges. The active compound concentration of the use forms can be from 0.0000001 up to 95% by weight of active compound, preferably between 0.0001 and 1% by weight.

They are applied in a customary manner adapted to suit the use forms.

When used against hygiene pests and stored-product pests, the active compound or active compound combinations is/are distinguished by excellent residual action on wood and clay as well as good stability to alkali on limed substrates.

As already mentioned above, it is possible to treat all plants and their parts in accordance with the invention. In a preferred embodiment, wild plant species or plant varieties and plant cultivars which have been obtained by traditional biological breeding methods, such as hybridization or protoplast fusion, and the parts of these varieties and cultivars are treated. In a further preferred embodiment, transgenic plants and plant cultivars which have been obtained by recombinant methods, if appropriate in combination with conventional methods (genetically modified organisms), and their parts are treated. The term "parts" or "parts of plants" or "plant parts" has been explained above.

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Plants which are treated particularly preferably in accordance with the invention are those of the plant cultivars which are in each case commercially available or in use. Plant cultivars are understood as meaning plants with new traits which have been bred either by conventional breeding, by mutagenesis or by recombinant DNA techniques. They may take the form of cultivars, biotypes and genotypes.

Depending on the plant species or plant cultivars, their location and growth conditions (soils, climate, vegetation period, nutrition), the treatment according to the invention may also result in superadditive ("synergistic") effects. Thus, for example, reduced application rates and/or a widened activity spectrum and/or an increase in the activity of the substances and compositions which can be used in accordance with the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to salinity in the water or soil, increased flowering performance, facilitated harvesting, accelerated maturation, higher yields, higher quality and/or better nutritional value of the harvested products, better storage characteristics and/or processibility of the harvested products are possible which exceed the effects which were actually to be expected.

The preferred transgenic plants or plant cultivars (those obtained by recombinant methods) to be treated in accordance with the invention include all those plants which, owing to the process of recombinant modification, were given genetic material which confers particular, advantageous, valuable traits to these plants. Examples of such properties are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to salinity in the water or soil, increased flowering performance, facilitated harvesting, accelerated maturation, higher yields, higher quality and/or higher nutritional value of the harvested products, better storage characteristics and/or processibility of the harvested products. Further examples of such traits, examples which must be mentioned especially, are better defence of the plants against animal and microbial pests, such as against insects, mites, phytopathogenic fungi, bacteria and/or viruses and an increased tolerance of the plants to certain herbicidal active compounds. Examples of transgenic plants which may be mentioned are the important crop plants, such as cereals (wheat, rice), maize, soya beans, potato, cotton, oilseed rape, beets, sugar cane and fruit plants (with the fruits apples, pears, citrus fruits and grapes), with particular emphasis on maize, soya beans, potatoes, cotton and oilseed rape. Traits which are especially emphasized are the increased defence of the plants against insects, owing to toxins being formed in the plants, in particular toxins which are generated in the plants by the genetic material of Bacillus thuringiensis (for

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example by the genes CryIA(a), CryIA(b), CryIA(c), CryIIA, CryIIIA, CryIIIB2, Cry9c, Cry2Ab, Cry3Bb and CryIF and their combinations; hereinbelow "Bt plants"). Other traits which are particularly emphasized are the increased defence of plants against fungi, bacteria and viruses by the systemic acquired resistance (SAR), systemin, phytoalexins, elicitors and resistance genes and correspondingly expressed proteins and toxins. Other traits which are especially emphasized are the increased tolerance of the plants to certain herbicidal active compounds, for example imidazolinones, sulphonylureas, glyphosate or phosphinothricin (for example "PAT" gene). The genes which confer the desired traits in each case may also be present in the transgenic plants in combination with one another. Examples of "Bt plants" which may be mentioned are maize cultivars, cotton cultivars, soya bean cultivars and potato cultivars which are commercially available under the trade names YIELD GARD® (for example maize, cotton, soya beans), KnockOut® (for example maize), StarLink® (for example maize), Bollgard® (cotton), Nucotn® (cotton) and NewLeaf® (potato). Examples of herbicide-tolerant plants which may be mentioned are maize cultivars, cotton cultivars and soya bean cultivars which are commercially available under the trade names Roundup Ready® (tolerance to glyphosate, for example maize, cotton, soya bean), Liberty Link® (tolerance to phosphinothricin, for example oilseed rape), IMI® (tolerance to imidazolinones) and STS® (tolerance to sulphonylureas, for example maize). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned include also the varieties commercially available under the name Clearfield® (for example maize). Naturally, these statements also apply to plant cultivars having these genetic traits or genetic traits still to be developed, which plant cultivars will be developed and/or marketed in the future.

The plants listed can be treated particularly advantageously with the compounds according to the invention or the active compound mixtures according to the invention. The preferred ranges stated above for the active compounds and mixtures also apply to the treatment of these plants. Particular emphasis may be given to the treatment of plants with the compounds or mixtures specifically mentioned in the present text.

The active compounds or active compound combinations according to the invention are not only active against plant, hygiene and stored-product pests, but also, in the veterinary medicine sector, against animal parasites (ectoparasites), such as ixodid ticks, argasid ticks, scab mites, trombiculid mites, flies (stinging and sucking), parasitic fly larvae, lice, hair lice, bird lice and fleas. These parasites include:

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From the order of the Anoplurida, for example, Haematopinus spp., Linognathus spp., Pediculus spp., Phtirus spp., Solenopotes spp.

From the order of the Mallophagida and the sub-orders Amblycerina and Ischnocerina, for example, Trimenopon spp., Menopon spp., Trinoton spp., Bovicola spp., Werneckiella spp., Lepikentron spp., Damalina spp., Trichodectes spp., Felicola spp.

From the order of the Diptera and the sub-orders Nematocerina and Brachycerina, for example, Aedes spp., Anopheles spp., Culex spp., Simulium spp., Eusimulium spp., Phlebotomus spp., Lutzomyia spp., Culicoides spp., Chrysops spp., Hybomitra spp., Atylotus spp., Tabanus spp., Haematopota spp., Philipomyia spp., Braula spp., Musca spp., Hydrotaea spp., Stomoxys spp., Haematobia spp., Morellia spp., Fannia spp., Glossina spp., Calliphora spp., Lucilia spp., Chrysomyia spp., Wohlfahrtia spp., Sarcophaga spp., Oestrus spp., Hypoderma spp., Gasterophilus spp., Hippobosca spp., Lipoptena spp. and Melophagus spp.

From the order of the Siphonapterida, for example, Pulex spp., Ctenocephalides spp.,

Xenopyslla spp. and Ceratophyllus spp.

From the order of the Heteropterida, for example, Cimex spp., Triatoma spp., Rhodnius spp. and Panstrongylus spp.

From the order of the Blattarida, for example, Blatta orientalis, Periplaneta americana, Blattella germanica and Supella spp.

From the sub-class of the Acaria (Acarida) and the orders of the Meta- and Mesostigmata, for example, Argas spp., Ornithodorus spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp., Haemophysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus spp., Raillietia spp., Pneumonyssus spp., Sternostoma spp. and Varroa spp.

From the order of the Actinedida (Prostigmata) and Acaridida (Astigmata), for example, Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergates spp., Demodex spp., Trombicula spp., Listrophorus spp., Acarus spp., Tyrophagus spp., Caloglyphus spp., Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp.,

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Otodectes spp., Sarcoptes spp., Notoedres spp., Knemidocoptes spp., Cytodites spp. and Laminosioptes spp.

The active compounds or active compound combinations according to the invention are also suitable for controlling arthropods which attack agricultural livestock, such as, for example, cattle, sheep, goats, horses, pigs, donkeys, camels, buffaloes, rabbits, chickens, turkeys, ducks, geese, honeybees, other domestic animals, such as, for example, dogs, cats, cage birds, aquarium fish, and so-called experimental animals, such as, for example, hamsters, guinea pigs, rats and mice. By combating these arthropods, it is intended to reduce deaths and decreased performances (in meat, milk, wool, hides, eggs, honey and the like), so that more economical and simpler animal keeping is made possible by using the active compounds according to the invention.

In the veterinary sector, the active compounds or active compound combinations according to the invention are used in a known manner by enteral administration, for example in the form of tablets, capsules, drinks, drenches, granules, pastes, boli, the feed-through method, suppositories, by parenteral administration, such as, for example, by means of injections (intramuscular, subcutaneous, intravenous, intraperitoneal and the like), implants, by nasal application, by dermal administration, for example in the form of dipping or bathing, spraying, pouring-on and spotting-on, washing, dusting, and with the aid of shaped articles which comprise active compound, such as collars, ear tags, tail marks, limb bands, halters, marking devices and the like.

When administered to livestock, poultry, domestic animals and the like, the active compounds or active compound combinations can be used as formulations (for example powders, emulsions, flowables) which comprise the active compounds in an amount of 1 to 80% by weight, either directly or after dilution by a factor of 100 to 10 000, or they may be used in the form of a chemical bath.

Furthermore, it has been found that the compounds or active compound combinations according to the invention have a potent insecticidal action against insects which destroy industrial materials.

The following insects may be mentioned by way of example and as being preferred, but without any limitation:

Beetles, such as

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Hylotrupes bajulus, Chlorophorus pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinus pecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthes rugicollis, Xyleborus spec., Tryptodendron spec., Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec., Dinoderus minutus.

Dermapterans, such as Sirex juvencus, Urocerus gigas, Urocerus gigas taignus, Urocerus augur.

Termites, such as Kalotermes flavicollis, Cryptotermes brevis, Heterotermes indicola, Reticulitermes flavipes, Reticulitermes santonensis, Reticulitermes lucifugus, Mastotermes darwiniensis, Zootermopsis nevadensis, Coptotermes formosanus.

Bristletails, such as Lepisma saccharina.

Industrial materials are to be understood as meaning, in the present context, non-live materials, such as, preferably, synthetic materials, glues, sizes, paper and board, leather, wood and timber products, and paint. The materials to be very particularly preferably protected against attack by insects are wood and timber products.

Wood and timber products which can be protected by the composition according to the invention or mixtures comprising such a composition are to be understood as meaning, for example:

construction timber, wooden beams, railway sleepers, bridge components, jetties, wooden vehicles, boxes, pallets, containers, telephone poles, wood cladding, windows and doors made of wood, plywood, particle board, joiner's articles, or wood products which, quite generally, are used in the construction of houses or in joinery.

The active compounds or active compound combinations can be used as such, in the form of concentrates or generally customary formulations, such as powders, granules, solutions, suspensions, emulsions or pastes.

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The formulations mentioned can be prepared in a manner known per se, for example by mixing the active compounds with at least one solvent or diluent, emulsifier, dispersant and/or binder or fixative, water repellent, if appropriate desiccants and UV stabilizers and, if appropriate, colorants and pigments and other processing auxiliaries. The insecticidal compositions or concentrates used for the protection of wood and wooden materials comprise the active compound according to the invention in a concentration of 0.0001 to 95% by weight, in particular 0.001 to 60% by weight.

The amount of the compositions or concentrates employed depends on the species and the occurrence of the insects and on the medium. The optimum rate of application can be determined upon use in each case by series of tests. However, in general, it suffices to employ 0.0001 to 20% by weight, preferably 0.001 to 10% by weight, of the active compound, based on the material to be protected.

The solvent and/or diluent used is an organochemical solvent or solvent mixture and/or an oily or oil-type organochemical solvent or solvent mixture of low volatility and/or a polar organochemical solvent or solvent mixture and/or water and, if appropriate, an emulsifier and/or wetting agent.

Organochemical solvents which are preferably employed are oily or oil-type solvents having an evaporation number of above 35 and a flashpoint of above 30°C, preferably above 45°C. Substances which are used as such oily and oil-type solvents which have low volatility and are insoluble in water are suitable mineral oils or their aromatic fractions, or mineral-oil-containing solvent mixtures, preferably white spirit, petroleum and/or alkylbenzene.

Substances which are advantageously used are mineral oils with a boiling range of 170 to 220°C, white spirit with a boiling range of 170 to 220°C, spindle oil with a boiling range of 250 to 350°C, petroleum or aromatics of boiling range 160 to 280°C, essence of turpentine and the like.

In a preferred embodiment, liquid aliphatic hydrocarbons with a boiling range of 180 to 210° C or high-boiling mixtures of aromatic and aliphatic hydrocarbons with a boiling range of 180 to 220° C and/or spindle oil and/or monochloronaphthalene, preferably α -monochloronaphthalene, are used.

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The organic oily or oil-type solvents of low volatility having an evaporation number of above 35 and a flashpoint of above 30°C, preferably above 45°C, can be partially replaced by organochemical solvents of high or medium volatility, with the proviso that the solvent mixture also has an evaporation number of above 35 and a flashpoint of above 30°C, preferably above 45°C, and that the insecticide/fungicide mixture is soluble or emulsifiable in this solvent mixture.

In a preferred embodiment, part of the organochemical solvent or solvent mixture is replaced or an aliphatic polar organochemical solvent or solvent mixture. Substances which are preferably used are aliphatic organochemical solvents having hydroxyl and/or ester and/or ether groups, such as, for example, glycol ethers, esters and the like.

The organochemical binders used within the scope of the present invention are the synthetic resins and/or binding drying oils which are known per se and can be diluted with water and/or are soluble or dispersible or emulsifiable in the organochemical solvents employed, in particular binders composed of, or comprising, an acrylate resin, a vinyl resin, for example polyvinyl acetate, polyester resin, polycondensation or polyaddition resin, polyurethane resin, alkyd resin or modified alkyd resin, phenol resin, hydrocarbon resin, such as indene/cumarone resin, silicone resin, drying vegetable and/or drying oils and/or physically drying binders based on a natural and/or synthetic resin.

The synthetic resin used as the binder can be employed in the form of an emulsion, dispersion or solution. Up to 10% by weight of bitumen or bituminous substances can also be used as binders. In addition, colorants, pigments, water repellents, odour-masking substances and inhibitors or anticorrosives known per se and the like can also be employed.

The composition or the concentrate preferably comprises, in accordance with the invention, at least one alkyd resin or modified alkyd resin and/or a drying vegetable oil as the organochemical binder. Preferably used according to the invention are alkyd resins with an oil content of over 45% by weight, preferably 50 to 68% by weight.

All or some of the abovementioned binder can be replaced by a fixative (mixture) or a plasticizer (mixture). These additives are intended to prevent volatilization of the active

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compounds and crystallization or precipitation. They preferably replace 0.01 to 30% of the binder (based on 100% of the binder employed).

The plasticizers are from the chemical classes of the phthalic esters, such as dibutyl phthalate, dioctyl phthalate or benzyl butyl phthalate, the phosphoric esters, such as tributyl phosphate, the adipic esters, such as di-(2-ethylhexyl) adipate, the stearates, such as butyl stearate or amyl stearate, the oleates, such as butyl oleate, the glycerol ethers or relatively high-molecular-weight glycol ethers, glycerol esters and p-toluenesulphonic esters.

Fixatives are chemically based on polyvinyl alkyl ethers, such as, for example, polyvinyl methyl ether, or ketones, such as benzophenone or ethylenebenzophenone.

Particularly suitable as a solvent or diluent is also water, if appropriate as a mixture with one or more of the abovementioned organochemical solvents or diluents, emulsifiers and dispersants.

Particularly effective protection of wood is achieved by large-scale industrial impregnation processes, for example vacuum, double-vacuum or pressure processes.

If appropriate, the ready-to-use compositions can additionally comprise other insecticides and, if appropriate, additionally one or more fungicides.

Suitable additional components which may be admixed are, preferably, the insecticides and fungicides mentioned in WO 94/29 268. The compounds mentioned in that document are expressly part of the present application.

Very particularly preferred components which may be admixed are insecticides, such as chlorpyriphos, phoxim, silafluofin, alphamethrin, cyfluthrin, cypermethrin, deltamethrin, permethrin, imidacloprid, NI-25, flufenoxuron, hexaflumuron, transfluthrin, thiacloprid, methoxyphenoxid and triflumuron,

and fungicides, such as epoxyconazole, hexaconazole, azaconazole, propiconazole, tebuconazole, cyproconazole, metconazole, imazalil, dichlofluanid, tolylfluanid, 3-iodo-2-propynylbutyl carbamate, N-octylisothiazolin-3-one and 4,5-dichloro-N-octylisothiazolin-3-one.

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The compounds or active compound combinations according to the invention can at the same time be employed for protecting objects which come into contact with salt water or brackish water, in particular hulls, screens, nets, buildings, moorings and signalling systems, against fouling.

Fouling by sessile Oligochaeta, such as Serpulidae, and by shells and species from the Ledamorpha group (goose barnacles), such as various Lepas and Scalpellum species, or by species from the Balanomorpha group (acorn barnacles), such as Balanus or Pollicipes species, increases the frictional drag of ships and, as a consequence, leads to a marked increase in operation costs owing to higher energy consumption and additionally frequent residence in the dry dock.

Apart from fouling by algae, for example Ectocarpus sp. and Ceramium sp., fouling by sessile Entomostraka groups, which come under the generic term Cirripedia (cirriped crustaceans), is of particular importance.

Surprisingly, it has now been found that the compounds according to the invention, alone or in combination with other active compounds, have an outstanding antifouling action.

Using the compounds according to the invention, alone or in combination with other active compounds, allows the use of heavy metals such as, for example, in bis(trialkyltin) sulphides, tri-n-butyltin laurate, tri-n-butyltin chloride, copper(I) oxide, triethyltin chloride, tri-n-butyl-(2-phenyl-4-chlorophenoxy)tin, tributyltin oxide, molybdenum disulphide, antimony oxide, polymeric butyl titanate, phenyl(bispyridine)bismuth chloride, tri-n-butyltin fluoride, manganese ethylenebisthiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisthiocarbamate, zinc salts and copper salts of 2-pyridinethiol 1-oxide, bisdimethyldithiocarbamate, copper thiocyanate, copper naphthenate and tributyltin halides to be dispensed with, or the concentration of these compounds to be substantially reduced.

If appropriate, the ready-to-use antifouling paints can additionally comprise other active compounds, preferably algicides, fungicides, herbicides, molluscicides, or other antifouling active compounds.

Preferably suitable components in combination with the antifouling compositions according to the invention are:

algicides such as

2-*tert*-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, dichlorophen, diuron, endothal, fentin acetate, isoproturon, methabenzthiazuron, oxyfluorfen, quinoclamine and terbutryn;

fungicides such as

benzo[b]thiophenecarboxylic acid cyclohexylamide S,S-dioxide, dichlofluanid, fluorfolpet, 3-iodo-2-propynyl butylcarbamate, tolylfluanid and azoles such as

azaconazole, cyproconazole, epoxyconazole, hexaconazole, metconazole, propiconazole and tebuconazole;

molluscicides such as

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fentin acetate, metaldehyde, methiocarb, niclosamid, thiodicarb and trimethacarb;

or conventional antifouling active compounds such as

- 4,5-dichloro-2-octyl-4-isothiazolin-3-one, diiodomethylparatryl sulphone, 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, potassium, copper, sodium and zinc salts of 2-pyridinethiol 1-oxide, pyridine-triphenylborane, tetrabutyldistannoxane, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, tetramethylthiuram disulphide and 2,4,6-trichlorophenylmaleimide.
- The antifouling compositions used comprise the active compounds according to the invention of the compounds according to the invention in a concentration of 0.001 to 50% by weight, in particular 0.01 to 20% by weight.

Moreover, the antifouling compositions according to the invention comprise the customary components such as, for example, those described in Ungerer, *Chem. Ind.* 1985, *37*, 730-732 and Williams, Antifouling Marine Coatings, Noyes, Park Ridge, 1973.

Besides the algicidal, fungicidal, molluscicidal active compounds and insecticidal active

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compounds according to the invention, antifouling paints comprise, in particular, binders.

Examples of recognized binders are polyvinyl chloride in a solvent system, chlorinated rubber in a solvent system, acrylic resins in a solvent system, in particular in an aqueous system, vinyl chloride/vinyl acetate copolymer systems in the form of aqueous dispersions or in the form of organic solvent systems, butadiene/styrene/acrylonitrile rubbers, drying oils such as linseed oil, resin esters or modified hardened resins in combination with tar or bitumens, asphalt and epoxy compounds, small amounts of chlorine rubber, chlorinated polypropylene and vinyl resins.

If appropriate, paints also comprise inorganic pigments, organic pigments or colorants which are preferably insoluble in salt water. Paints may furthermore comprise materials such as rosin to allow controlled release of the active compounds. Furthermore, the paints may comprise plasticizers, modifiers which affect the rheological properties and other conventional constituents. The compounds according to the invention or the abovementioned mixtures may also be incorporated into self-polishing antifouling systems.

The active compounds or active compound combinations are also suitable for controlling animal pests, in particular insects, arachnids and mites, which are found in enclosed spaces such as, for example, dwellings, factory halls, offices, vehicle cabins and the like. They can be employed in domestic insecticide products for controlling these pests alone or in combination with other active compounds and auxiliaries. They are active against sensitive and resistant species and against all development stages. These pests include:

From the order of the Scorpionidea, for example, Buthus occitanus.

From the order of the Acarina, for example, Argas persicus, Argas reflexus, Bryobia ssp., Dermanyssus gallinae, Glyciphagus domesticus, Ornithodorus moubat, Rhipicephalus sanguineus, Trombicula alfreddugesi, Neutrombicula autumnalis, Dermatophagoides pteronissimus, Dermatophagoides forinae.

From the order of the Araneae, for example, Aviculariidae, Araneidae.

From the order of the Opiliones, for example, Pseudoscorpiones chelifer, Pseudoscorpiones cheiridium, Opiliones phalangium.

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From the order of the Isopoda, for example, Oniscus asellus, Porcellio scaber.

From the order of the Diplopoda, for example, Blaniulus guttulatus, Polydesmus spp.

5 From the order of the Chilopoda, for example, Geophilus spp.

From the order of the Zygentoma, for example, Ctenolepisma spp., Lepisma saccharina, Lepismodes inquilinus.

From the order of the Blattaria, for example, Blatta orientalis, Blattella germanica, Blattella asahinai, Leucophaea maderae, Panchlora spp., Parcoblatta spp., Periplaneta australasiae, Periplaneta americana, Periplaneta brunnea, Periplaneta fuliginosa, Supella longipalpa.

From the order of the Saltatoria, for example, Acheta domesticus.

From the order of the Dermaptera, for example, Forficula auricularia.

From the order of the Isoptera, for example, Kalotermes spp., Reticulitermes spp.

15 From the order of the Psocoptera, for example, Lepinatus spp., Liposcelis spp.

From the order of the Coleptera, for example, Anthrenus spp., Attagenus spp., Dermestes spp., Latheticus oryzae, Necrobia spp., Ptinus spp., Rhizopertha dominica, Sitophilus granarius, Sitophilus oryzae, Sitophilus zeamais, Stegobium paniceum.

From the order of the Diptera, for example, Aedes aegypti, Aedes albopictus, Aedes taeniorhynchus, Anopheles spp., Calliphora erythrocephala, Chrysozona pluvialis, Culex quinquefasciatus, Culex pipiens, Culex tarsalis, Drosophila spp., Fannia canicularis, Musca domestica, Phlebotomus spp., Sarcophaga carnaria, Simulium spp., Stomoxys calcitrans, Tipula paludosa.

From the order of the Lepidoptera, for example, Achroia grisella, Galleria mellonella, Plodia 25 interpunctella, Tinea cloacella, Tinea pellionella, Tineola bisselliella.

From the order of the Siphonaptera, for example, Ctenocephalides canis, Ctenocephalides felis, Pulex irritans, Tunga penetrans, Xenopsylla cheopis.

From the order of the Hymenoptera, for example, Camponotus herculeanus, Lasius fuliginosus, Lasius niger, Lasius umbratus, Monomorium pharaonis, Paravespula spp., Tetramorium caespitum.

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From the order of the Anoplura, for example, Pediculus humanus capitis, Pediculus humanus corporis, Phthirus pubis.

From the order of the Heteroptera, for example, Cimex hemipterus, Cimex lectularius, Rhodinus prolixus, Triatoma infestans.

They are used in the household insecticides sector alone or in combination with other suitable active compounds such as phosphoric esters, carbamates, pyrethroids, growth regulators or active compounds from other known classes of insecticides.

They are used in aerosols, pressure-free spray products, for example pump and atomizer sprays, automatic fogging systems, foggers, foams, gels, evaporator products with evaporator tablets made of cellulose or polymer, liquid evaporators, gel and membrane evaporators, propeller-driven evaporators, energy-free, or passive, evaporation systems, moth papers, moth bags and moth gels, as granules or dusts, in baits for spreading or in bait stations.

The active compounds or active compound combinations according to the invention can also be used as defoliants, desiccants, haulm killers and, in particular, as weed killers. Weeds in the broadest sense are understood as meaning all plants which grow at locations where they are undesired. Whether the substances according to the invention act as nonselective or selective herbicides depends essentially on the application rate.

The active compounds or active compound combinations according to the invention can be used for example in the following plants:

Dicotyledonous weeds of the genera: Abutilon, Amaranthus, Ambrosia, Anoda, Anthemis, Aphanes, Atriplex, Bellis, Bidens, Capsella, Carduus, Cassia, Centaurea, Chenopodium, Cirsium, Convolvulus, Datura, Desmodium, Emex, Erysimum, Euphorbia, Galeopsis, Galinsoga, Galium, Hibiscus, Ipomoea, Kochia, Lamium, Lepidium, Lindernia, Matricaria,

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Mentha, Mercurialis, Mullugo, Myosotis, Papaver, Pharbitis, Plantago, Polygonum, Portulaca, Ranunculus, Raphanus, Rorippa, Rotala, Rumex, Salsola, Senecio, Sesbania, Sida, Sinapis, Solanum, Sonchus, Sphenoclea, Stellaria, Taraxacum, Thlaspi, Trifolium, Urtica, Veronica, Viola, Xanthium.

5 <u>Dicotyledonous crops of the genera:</u> Arachis, Beta, Brassica, Cucumis, Cucurbita, Helianthus, Daucus, Glycine, Gossypium, Ipomoea, Lactuca, Linum, Lycopersicon, Nicotiana, Phaseolus, Pisum, Solanum, Vicia.

Monocotyledonous weeds of the genera: Aegilops, Agropyron, Agrostis, Alopecurus, Apera, Avena, Brachiaria, Bromus, Cenchrus, Commelina, Cynodon, Cyperus, Dactyloctenium, Digitaria, Echinochloa, Eleocharis, Eleusine, Eragrostis, Eriochloa, Festuca, Fimbristylis, Heteranthera, Imperata, Ischaemum, Leptochloa, Lolium, Monochoria, Panicum, Paspalum, Phalaris, Phleum, Poa, Rottboellia, Sagittaria, Scirpus, Setaria, Sorghum.

Monocotyledonous crops of the genera: Allium, Ananas, Asparagus, Avena, Hordeum, Oryza, Panicum, Saccharum, Secale, Sorghum, Triticale, Triticum, Zea.

However, the use of the active compounds or active compound combinations according to the invention is in no way restricted to these genera, but extends in the same manner to other plants.

Depending on the concentration, the active compounds or active compound combinations according to the invention are suitable for the nonselective weed control on, for example, industrial terrains and railway tracks and on paths and locations with and without trees. Likewise the active compounds according to the invention can be employed for controlling weeds in perennial crops, for example forests, ornamental tree plantings, orchards, vineyards, citrus groves, nut orchards, banana plantations, coffee plantations, tea plantations, rubber plantations, oil palm plantations, cocoa plantations, soft fruit plantings and hop fields, on lawns, turf and pastureland, and for the selective control of weeds in annual crops.

The compounds or active compound combinations according to the invention have strong herbicidal activity and a broad activity spectrum when used on the soil and on aerial plant parts. To a certain extent, they are also suitable for the selective control of

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monocotyledonous and dicotyledonous weeds in monocotyledonous and dicotyledonous crops, both pre- and post-emergence.

At certain concentrations or application rates, the active compounds or active compound combinations according to the invention can also be employed for controlling animal pests and fungal or bacterial plant diseases. If appropriate, they can also be used as intermediates or precursors for the synthesis of other active compounds.

The active compounds or active compound combinations can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, pastes, soluble powders, granules, suspension concentrates, natural and synthetic materials impregnated with active compound, and microcapsules in polymeric substances.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is liquid solvents and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants and/or foam-formers.

If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatics, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols, such as butanol or glycol, and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water.

Suitable solid carriers are: for example ammonium salts and ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly disperse silica, alumina and silicates, suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, and also synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam-formers are: for example non-ionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl

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polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and protein hydrolysates; suitable dispersants are: for example lignosulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, and also natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention, as such or in their formulations, can also be used for weed control purposes as a mixture with known herbicides and/or with substances which improve crop plant compatibility ("safeners"), ready mixes or tank mixes being possible. Mixtures with herbicide products which contain one or more known herbicides and a safener are hence also possible.

Herbicides which are suitable for the mixtures are known herbicides, for example

acetochlor, acifluorfen (-sodium), aclonifen, alachlor, alloxydim (-sodium), ametryne, azafenidin, amidosulfuron, anilofos, asulam, atrazine, amidochlor, amicarbazone, azimsulfuron, beflubutamid, benazolin (-ethyl), benfuresate, bensulfuron (-methyl), bentazone, benzefendizone, benzobicyclon, benzofenap, benzoylprop (-ethyl), bialaphos, bifenox, bispyribac (-sodium), bromobutide, bromofenoxim, bromoxynil, butachlor, butafenacil (-allyl), butroxydim, butylate, cafenstrole, caloxydim, carbetamide, carfentrazone (-ethyl), chlomethoxyfen, chloramben, chloridazon, chlorimuron (-ethyl), chlornitrofen, chlorsulfuron, chlortoluron, cinidon (-ethyl), cinmethylin, cinosulfuron, clefoxydim, clethodim, clodinafop (-propargyl), clomazone, clomeprop, clopyralid, clopyrasulfuron cycloate, cybutryne, (-methyl), cumyluron, cyanazine, cloransulam (-methyl), cyclosulfamuron, cycloxydim, cyhalofop (-butyl), 2,4-D, 2,4-DB, desmedipham, diallate,

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dicamba, dichlorprop (-P), diclofop (-methyl), diclosulam, diethatyl (-ethyl), difenzoquat, dimepiperate, dimethachlor, dimethametryn, diflufenzopyr, dimefuron, diflufenican. dimethenamid, dimexyflam, dinitramine, diphenamid, diquat, dithiopyr, diuron, dymron, epropodan, EPTC, esprocarb, ethalfluralin, ethametsulfuron (-methyl), ethofumesate, ethoxyfen, ethoxysulfuron, etobenzanid, fenoxaprop (-P-ethyl), fentrazamide, flamprop (isopropyl, -isopropyl-L, -methyl), flazasulfuron, florasulam, fluazifop (-P-butyl), fluazolate, flucarbazone (-sodium), flufenacet, flumetsulam, flumiclorac (-pentyl), flumioxazin, flumetsulam, fluometuron, fluorochloridone, fluoroglycofen (-ethyl), flumipropyn, flupoxam, flupropacil, flurpyrsulfuron (-methyl, -sodium), flurenol (-butyl), fluridone, fluroxypyr (-butoxypropyl, -meptyl), flurprimidol, flurtamone, fluthiacet (-methyl), fluforamsulfuron, glufosinate (-ammonium), glyphosate thiamide, fomesafen, (-isopropylammonium), halosafen, haloxyfop (-ethoxyethyl, -P-methyl), hexazinone, imazamethabenz (-methyl), imazamethapyr, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, iodosulfuron (-methyl, -sodium), ioxynil, isopropalin, isoproturon, isouron, isoxaben, isoxachlortole, isoxaflutole, isoxapyrifop, lactofen, lenacil, linuron, MCPA, mecoprop, mefenacet, mesosulfurone, metamitron, mesotrione, metazachlor, methabenzthiazuron, metobenzuron, metobromuron, (alpha-) metolachlor, metosulam, metoxuron, metribuzin, metsulfuron (-methyl), molinate, monolinuron, naproanilide, napropamide, neburon, nicosulfuron, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxaziclomefone, oxyfluorfen, paraquat, pelargonic acid, pendimethalin, pendralin, pentoxazone, phenmedipham, picolinafen, pinoxaden, piperophos, pretilachlor, primisulfuron (-methyl), profluazol, prometryn, propachlor, propanil, propaquizafop, propisochlor, propoxycarbazone (-sodium), propyzamide, prosulfocarb, pyrazolate, pyrazosulfuron pyraflufen (-ethyl), pyrazogyl, prosulfuron, (-ethyl), pyrazoxyfen, pyribenzoxim, pyributicarb, pyridate, pyridatol, pyriftalide, pyriminobac (-methyl), pyrithiobac (-sodium), quinchlorac, quinmerac, quinoclamine, quizalofop (-P-ethyl, -P-tefuryl), rimsulfuron, sethoxydim, simazine, simetryn, sulcotrione, sulfentrazone, sulfometuron (-methyl), sulfosate, sulfosulfuron, tebutam, tebuthiuron, tepraloxydim, terbuthylazine, terbutryn, thenylchlor, thiafluamide, thiazopyr, thidiazimin, thifensulfuron (-methyl), thiobencarb, tiocarbazil, tralkoxydim, triallate, triasulfuron, tribentrifloxysulfuron. triflusulfuron trifluralin, triclopyr, tridiphane, uron (-methyl), (-methyl), tritosulfuron.

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A mixture with other known active compounds, such as fungicides, insectides, acaricides, nematicides, bird repellents, plant nutrients and soil conditioners, is also possible.

The active compounds or active compound combinations can be applied as such, in the form of their formulations or the use forms prepared therefrom by further dilution, such as ready-to-use solutions, suspensions, emulsions, powders, pastes and granules. They are applied in the customary manner, for example by watering, spraying, atomizing, scattering.

The active compounds or active compound combinations according to the invention can be applied both before and after plant emergence. They can also be incorporated into the soil prior to sowing.

The application rate of active compound can vary within a substantial range. Essentially, it depends on the nature of the desired effect. In general, the application rates are between 1 g and 10 kg of active compound per hectare of soil area, preferably between 5 g and 5 kg per ha.

The advantageous effect of the compatibility with crop plants of the active compound combinations according to the invention is particularly pronounced at certain concentration ratios. However, the weight ratios of the active compounds in the active compound combinations can be varied within relatively wide ranges. In general, from 0.001 to 1000 parts by weight, preferably from 0.01 to 100 parts by weight, particularly preferably 0.05 to 20 parts by weight, of one of the compounds which improves crop plant compatibility (antidotes/safeners) mentioned above under (b') are present per part by weight of active compound of the formula (I).

The active compound combinations according to the invention are generally applied in the form of finished formulations. However, the active compounds contained in the active compound combinations can, as individual formulations, also be mixed during use, i.e. be applied in the form of tank mixes.

For certain applications, in particular by the post-emergence method, it may furthermore be advantageous to include, as further additives in the formulations, mineral or vegetable oils which are compatible with plants (for example the commercial preparation "Rako Binol"), or ammonium salts, such as, for example, ammonium sulphate or ammonium thiocyanate.

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The novel active compound combinations can be used as such, in the form of their formulations or the use forms prepared therefrom by further dilution, such as ready-to-use solutions, suspensions, emulsions, powders, pastes and granules. Application is in the customary manner, for example by watering, spraying, atomizing, dusting or scattering.

The application rates of the active compound combinations according to the invention can be varied within a certain range; they depend, inter alia, on the weather and on soil factors. In general, the application rates are between 0.001 and 5 kg per ha, preferably between 0.005 and 2 kg per ha, particularly preferably between 0.01 and 0.5 kg per ha.

The active compound combinations according to the invention can be applied before and after emergence of the plants, that is to say by the pre-emergence and post-emergence method.

Depending on their properties, the safeners to be used according to the invention can be used for pretreating the seed of the crop plant (seed dressing) or can be introduced into the seed furrows prior to sowing or be used separately prior to the herbicide or together with the herbicide, before or after emergence of the plants.

Preparation and use of the active compounds according to the invention are illustrated in the examples below.

Preparation Examples

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Example No. I-a-1 Process A

129.3 g (1.076 mol) of potassium tert-butoxide in 350 ml of anhydrous dimethylformamide (DMF) are initially charged in a 21 three-necked flask; at 20 to 40°C, 208.5 g of the compound according to Ex. II-1 in 420 ml of anhydrous dimethylformamide are added dropwise. The reaction mixture is stirred at 45°C for 80 min and then poured into 3500 ml of ice-water and, at 0-10°C, acidified with conc. hydrochloric acid to pH 2, and the precipitate is filtered off with suction, washed with ice-water and dried.

Yield: 183.55 g (95% of theory), m.p.: 305°C (content according to HPLC 99.6%).

Example No. I-a-1 Process I

$$CH_3O$$
 OH
 H_3C
 C_2H_5
 Br

2.8 g (0.023 mol) of potassium tert-butoxide are initially charged in 8 ml of anhydrous dimethylformamide. At 20-40°C, 4.54 g of a 65:35 cis/trans isomer mixture according to Example II-1, which was obtained by the process described in EP-A 835 243 for preparing compounds of the formula II, in 9 ml of anhydrous DMF are added dropwise, and the mixture is stirred at 40°C and monitored by thin-layer chromatography. 90 ml of ice-water are then added, using conc. HCl, the mixture is, at 0-10°C, acidified to pH 2, and the precipitate is filtered off with suction and washed with ice-water. The product is dried and purified by silica gel column chromatography (dichloromethane/acetone, 5:1)

Yield: 1.61 g (38% of theory)

Content according to HPLC (purity of 97.8%), cis/trans ratio of 92.3:7.7.

The following compounds of the formula (I-a) are obtained analogously to Example (I-a-1) and in accordance with the statements on the preparation:

$$AO \bigvee_{OH} \bigvee_{Z} \bigvee_{Y} (I-a)$$

Ex. No.	X	Y	Z	A	m.p.°C
I-a-2	C ₂ H ₅	Cl	CH ₃	CH ₃	293
I-a-3	C ₂ H ₅	Br	C ₂ H ₅	CH ₃	* 1.01 (t, 3H, CH ₂ CH ₃) 2.38 (q, 2H, CH ₂ CH ₃) 3.12 (m, 1H, CH-OCH ₃
I-a-4	C ₂ H ₅	Cl	C ₂ H ₅	CH ₃	247

* ¹H-NMR (300 MHz, CDCl₃), shift δ in ppm

Example No. I-b-1

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$$H_3C$$
 O
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5

204 mg (0.5 mmol) of the compound of Example I-1-a-44 (EP-A-835 243) and 56 mg (0.55 mmol) of triethylamine in 8 ml of ethyl acetate are heated under reflux, and a solution of 60 mg (0.55 mmol) of methoxyacetyl chloride in 2 ml of ethyl acetate is slowly added dropwise. The mixture is stirred under reflux for a further 4 h. 5 ml of NaCl solution are added to the reaction solution, and the organic phase is extracted with ethyl acetate. The aqueous phase is adjusted to pH 7 using NaHCO₃ solution and extracted with ethyl acetate.

The organic phases are combined and dried and the solvent is distilled off. The residue is purified by column chromatography on silica gel (100% ethyl acetate).

Yield: 76.6 mg (31.8%), m.p. 171-172°C.

The following compounds of the formula (I-b) are obtained analogously to Example (I-b-1)
and in accordance with the general statements on the preparation and separation:

$$A-O \xrightarrow{H} \xrightarrow{X} (I-b)$$

Ex. No.	X	Y	Z	A	R ¹	m.p.°C
I-b-2	C ₂ H ₅	Br	CH ₃	CH ₃	t-C ₄ H ₉	198
I-b-3	C ₂ H ₅	Br	CH ₃	CH ₃	H ₃ C-O-CH ₂	158-159
I-b-4	C ₂ H ₅	Br	CH ₃	CH ₃	H ₅ C ₂ -O-CH ₂	142
I-b-5	C ₂ H ₅	Br	CH ₃	CH ₃	i-C₃H ₇	195-197
I-b-6	C ₂ H ₅	Br	CH ₃	C ₂ H ₅	i-C ₃ H ₇	178
I-b-7	C ₂ H ₅	Br	CH₃	C ₂ H ₅	H₃C-O-CH₂	*2.49 (m, 2H, <u>CH</u> ₂ - Ar) 3.99 (dq, 2H, - <u>CH</u> ₂ -O)
I-b-8	C ₂ H ₅	CI	CH₃	CH ₃	i-C ₃ H ₇	*1.00 (t, 6H, CH(CH ₃) ₂) 3.35 (s, 3H, -O <u>C</u> H ₃)

^{* &}lt;sup>1</sup>H-NMR (300 MHz, CDCl₃):

10 shift δ in ppm

Example No. I-c-1 Process (I)

At 10-20°C, 0.2 ml (2 mmol) of ethyl chloroformate in 5 ml of anhydrous dichloromethane are added to a solution of 0.781 g (0.002 mol) of the compound of Example I-a-1 (obtained according to Process I) in 20 ml of anhydrous dichloromethane and 0.28 ml (2 mmol) of triethylamine. The mixture is stirred at room temperature and the reaction is monitored by thin-layer chromatography. The reaction mixture is washed twice with 10 ml of 0.5N NaOH solution. After drying, the solvent is distilled off. The product is then purified chromatographically on silica gel (dichloromethane/ethyl acetate, 3:1).

Yield: 0.7 g (77% of theory), m.p. 175°C.

Content according to HPLC 97.3%

Example I-c-1 (Process C)

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In a 21 three-necked flask, 14 ml (100 mmol) of triethylamine are added to 39.4 g (0.1 mol) of the compound of Example I-a-1 (Process A) in 1000 ml of anhydrous dichloromethane, and 10 ml (100 mmol) of ethyl chloroformate in 100 ml of anhydrous dichloromethane are added at 10-20°C. The mixture is stirred at room temperature and the reaction is monitored by thin-layer chromatography. The mixture is washed 2 × with 200 ml of 0.5N NaOH and

dried, and the solvent is distilled off. The residue was recrystallized from 150 ml of MTB ether and 150 ml of n-hexane.

Yield: 34.05 g (73% of theory), m.p. 179°C.

Content according to HPLC 100%.

5 The following compounds of the formula (I-c) are obtained analogously to Example (I-c-1) and in accordance with the general statements on the preparation:

Ex. No.	X	Y	Z	A	M	R ²	m.p.°C
I-c-2	C ₂ H ₅	Br	C ₂ H ₅	CH ₃	0	C ₂ H ₅	1H-NMR (300 MHz; CDCl ₃) δ=3.24 (m, 1H, <u>CH</u> -OCH ₃) ppm.:
I-c-3	C ₂ H ₅	Br	CH ₃	CH ₃	0	CH ₂ =CH-CH ₂ -	171
I-c-4	C ₂ H ₅	Cl	CH ₃	CH ₃	0	C ₂ H ₅	112-113

Example No. II-1

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237 ml (3.113 mol) of thionyl chloride are added to 160 g of 2-ethyl-4-bromo-6-methylphenylacetic acid (EP-A-835 243, Ex. XXV-3). The mixture is stirred at 80°C until the evolution of gas has ceased. At 50°C, excess thionyl chloride is removed using a rotary evaporator, 400 ml of anhydrous toluene are added and the mixture is again concentrated

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using a rotary evaporator. The residue is taken up in 250 ml of anhydrous acetonitrile (solution 1). 160 g of methyl cis-4-methoxy-1-aminocyclohexanecarboxylate hydrochloride (known from EP-A-1 309 562; Ex. 15) (0.653 mol), 91% pure, in 630 ml of anhydrous acetonitrile are initially charged in a 21 three-necked flask, and 286.4 g (2.054 mol) of ground potassium carbonate are added. At 0-10°C, solution 1 is added dropwise. The mixture is stirred at room temperature for 1 hour. The reaction solution is poured into 5000 ml of ice-water and filtered off with suction, and the residue is taken up in 11 of CH₂Cl₂, washed with 300 ml of 1N HCl, dried, concentrated using a rotary evaporator and crystallized from MTB ether/n-hexane. This gives 157 g (HPLC 100%). The mother liquor was concentrated and again recrystallized from MTB ether/n-hexane, 44.5 g (HPLC 97%). After homogenization of the batches, the product was used for preparing Example I-a-1 (Process A).

¹H-NMR (400 MHz, CDCl₃): δ = 1.22 (t, 3H, CH₂CH₃), 2.31 (s, 3H, ArCH₃), 3.14 (m, 1H, CHOCH₃), 3.31 (s, 3H, CHOCH₃), 3.51 (s, 2H, CO-CH₂), 3.69 (s, 3H, CO₂CH₃) ppm.

15 The following compounds of the formula (II) are obtained analogously to Example (II-1) and in accordance with the statements on the preparation

$$A-O$$
 CO_2R^8
 Z
(II)

Ex. No.	X	Y	Z	A	R ⁸	m.p.°C
II-2	C ₂ H ₅	Cl	CH ₃	CH ₃	CH ₃	* 3.16 (m, 1H, <u>CH</u> OCH ₃) 3.51 (s, 3H, CO ₂ <u>CH₃</u>)
II-3	C ₂ H ₅	Br	C ₂ H ₅	CH ₃	CH₃	+ 3.31 (s, 3H, O <u>CH</u> ₃) 3.68 (s, 3H, CO ₂ <u>CH</u> ₃

- * ¹H-NMR (400 MHz, d₆ DMSO); shift δ in ppm
- + ¹H-NMR (300 MHz, CDCl₃); shift δ in ppm

Use Examples

Example A

Meloidogyne Test

Solvent:

7 parts by weight of dimethylformamide

5 Emulsifier:

2 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

Vessels are filled with sand, solution of active compound, Meloidogyne incognita egg/larvae suspension and lettuce seeds. The lettuce seeds germinate and the plants develop. On the roots, the galls develop.

After the desired period of time, the nematicidal action is determined in % by the formation of galls. 100% means that no galls have been found; 0% means that the number of galls on the treated plants corresponds to that of the untreated control.

In this test, for example, the following compound of the Preparation Examples shows good activity:

Table A

plant-damaging nematodes

Meloidogyne Test

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Active compounds	Concentration of active	Effect
	compound in ppm	in % after 14 ^d
Ex. I-c-1	20	90

Example B

Myzus Test (spray treatment)

Solvents:

78 parts by weight of acetone

1.5 parts by weight of dimethylformamide

5 Emulsifier:

0.5 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Discs of Chinese cabbage (Brassica pekinensis) which are infested by all stages of the green peach aphid (Myzus persicae) are sprayed with a preparation of active compound of the desired concentration.

After the desired period of time, the activity in % is determined. 100% means that all aphids have been killed; 0% means that none of the aphids have been killed.

In this test, for example, the following compound of the Preparation Examples shows good activity:

Table B

plant-damaging insects

Myzus Test

Active compounds	Concentration of active	Kill rate
	compound in g/ha	in % after 5d
Ex. I-c-1	100	90

Example C

Phaedon Test (spray treatment)

Solvent:

78 parts by weight of acetone

1.5 parts by weight of dimethylformamide

5 Emulsifier:

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0.5 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Discs of Chinese cabbage (Brassica pekinensis) are sprayed with a preparation of active compound of the desired concentration and, after they have dried, populated with larvae of the mustard beetle (Phaedon cochleariae).

After the desired period of time, the activity in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed.

In this test, for example, the following compound of the Preparation Examples shows good activity:

Table C

plant-damaging insects

Phaedon Test

Active compounds	Concentration of active	Kill rate
·	compound in g/ha	in % after 7d
Ex. I-c-1	100	83

Example D

Tetranychus Test (OP-resistant/spray treatment)

Solvent:

- 78 parts by weight of acetone
- 1.5 parts by weight of dimethylformamide

5 Emulsifier:

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0.5 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Discs of bean leaves (*Phaseolus vulgaris*) which are infested by all stages of the greenhouse red spider mite (*Tetranychus urticae*) are sprayed with a preparation of active compound of the desired concentration.

After the desired period of time, the activity in % is determined. 100% means that all spider mites have been killed; 0% means that none of the spider mites have been killed.

In this test, for example, the following compound of the Preparation Examples shows good activity:

Table D

plant-damaging mites

Tetranychus Test (OP-resistant/spray treatment)

Active compounds	Concentration of active	Kill rate
	compound in g/ha	in % after 5 ^d
Ex. I-c-1	100	70

Example E

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1. Herbicidal pre-emergence action

Seeds of monocotyledonous and dicotyledonous weed and crop plants are placed into sandy loam in wood fibre pots and covered with soil. The test compounds, formulated in the form of wettable powders (WP), are then, in various dosages as aqueous suspension with a water application rate of 600 l/ha (converted), with 0.2% of wetting agent added, applied to the surface of the covering soil.

After the treatment, the pots are placed in a greenhouse and kept under good growth conditions for the test plants. The visual assessment of the emergence damage on the test plants is carried out after a trial period of 3 weeks by comparison with untreated plants (herbicidal effect in per cent (%): 100% effect = the plants have died, 0% effect = like control plants).

2. Herbicidal post-emergence action

Seeds of monocotyledonous and dicotyledonous weed and crop plants are placed into sandy loam in wood fibre pots, covered with soil and cultivated in a greenhouse under good growth conditions. 2-3 weeks after sowing, the test plants are treated at the one-leaf stage. The test compounds, formulated as wettable powders (WP), are, in various dosages with a water application rate of 600 l/ha (converted), with 0.2% of wetting agent added, sprayed onto the green parts of the plants. After the test plants were kept in the greenhouse under optimum growth conditions for about 3 weeks, the effect of the preparations is rated visually in comparison to untreated controls (herbicidal effect in per cent (%): 100% effect = the plants have died, 0% effect = like control plants).

Greenhouse		g a.i./ha	Sugar-	Agropy	ron Alope	ecur- A	vena	Lolium	Setaria
			beets		u:	S			
Ex. I-c-1	pre-	320	0	100	10	0	97	100	100
	emergence				-				
	post-	320	0	100	10	0	100	100	100
	emergence								
Greenhouse		g a.i./ha	Sugar-	Avena	Digitaria	Lolium	Setaria	Abutilon	Veronica
			beets						
Ex. I-b-3	pre-	320	0	80	100	100	100	-	100
	emergence								
	post-	320	0	100	100	100	100	70	-
	emergence								
Greenhouse		g a.i./ha	Sugar-	Avena	Digitaria	Lolium	Setaria	ı	
			beets						
Ex. I-c-2	pre-	320	0	80	100	100	100	_	
	emergence								
	post-	320	0	100	100	100	100		
	emergence								

Example F

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1. Herbicidal post-emergence action

Seeds of monocotyledonous and dicotyledonous weed and crop plants are placed in sandy loam in wood fibre pots or in plastic pots, covered with soil and cultivated in a greenhouse, during the vegetation period also outdoors outside of the greenhouse, under good growth conditions. 2-3 weeks after sowing, the test plants are treated at the one- to three-leaf stage. The test compounds, formulated as wettable powders (WP) or emulsifiable concentrates (EC) are, in various dosages with a water application rate of 300 l/ha (converted), with wetting agent (0.2 to 0.3%) added, sprayed onto the plants and the surface of the soil. 3-4 weeks after the treatment of the test plants, the effect of the preparations is rated visually in comparison to untreated controls (herbicidal effect in per cent (%): 100% effect = the plants have died, 0% effect = like control plants).

Use of safeners

If it is additionally to be tested whether safeners can improve the plant compatibility of test substances in the case of crop plants, the following options are used for applying the safener:

- seeds of the crop plants are, before sowing, dressed with the safener substance (the amount of safener is stated in per cent, based on the weight of the seed)
- before the application of the test substances, the crop plants are sprayed with the safener at a certain application rate per hectar (usually 1 day before the application of the test substances)
 - the safener is applied together with the test substance as a tank mix (the amount of safener is stated in g/ha or as a ratio, based on the herbicide).

By comparing the effect of test substances on crop plants with or without safener treatment, it is possible to assess the effect of the safener substance.

Container trials with cereals outdoors (outside the greenhouse/"bird cage") Mefenpyr in tank mix

	Application rate	Summer barley	Summer wheat
	g of a.i./ha	observed (%)	observed (%)
Ex. I-c-1	120	35	20
Ex. I-c-1	120 + 240	0	5
+ Mefenpyr			

	Application rate	Summer barley	Summer wheat
	g of a.i./ha	observed (%)	observed (%)
Ex. I-a-1	120	35	30
Ex. I-a-1	120 + 240	5	10
+ Mefenpyr			

	Application rate	Summer wheat
	g of a.i./ha	observed (%)
Ex. I-a-2	120	50
Ex. I-a-2	120 + 240	25
+ Mefenpyr		

Container trials with cereals in the greenhouse Mefenpyr applied 1 day prior to the application of herbicide

	Application rate	Summer barley
	g of a.i./ha	observed (%)
Ex. I-b-1	50	50
Ex. I-b-1	50 + 100	25
+ Mefenpyr		

	Application rate	Summer wheat
	g of a.i./ha	observed (%)
Ex. I-b-4	12.5	80
Ex. I-b-4	12.5 + 100	30
+ Mefenpyr	-	

Example G

Critical concentration test/soil insects - treatment of transgenic plants

Test insect:

Diabrotica balteata – larvae in soil

Solvent:

7 parts by weight of acetone

5 Emulsifier:

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1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

The preparation of active compound is poured onto the soil. Here, the concentration of active compound in the preparation is virtually immaterial, only the amount by weight of active compound per volume unit of soil, which is stated in ppm (mg/l), matters. The soil is filled into 0.25 l pots, and they are allowed to stand at 20°C.

Immediately after the preparation, 5 pregerminated maize corns of the cultivar YIELD GUARD (trademark of Monsanto Comp., USA) are placed into each pot. After 2 days, the appropriate test insects are placed into the treated soil. After a further 7 days, the efficacy of the active compound is determined by counting the maize plants that have emerged (1 plant = 20% activity).

Example H

Heliothis virescens test – treatment of transgenic plants

Solvent:

7 parts by weight of acetone

Emulsifier:

1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

Soya bean shoots (Glycine max) of the cultivar Roundup Ready (trademark of Monsanto Comp. USA) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with the tobacco bud worm Heliothis virescens while the leaves are still moist.

After the desired period of time, the kill of the insects is determined.